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CHEMISTRY

FOR

AGRICULTURAL STUDENTS

BY

R. H. ADIE, M.A., B.Sc.

SOMETIME LECTURER IN CHEMISTRY, ST. JOHN'S COLLEGE, CAMBRIDGE
LECTURER IN PHYSICS AND CHEMISTRY, SCHOOL OF AGRICULTURE, CAMBRIDGE

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PREFACE.

In the application of research to agricultural problems a very wide acquaintance with many branches of scientific work is necessary, and the Honours student should be capable of applying his knowledge of the scientific methods of his special branch to the study of other branches. The ordinary student of agriculture cannot spare time for advanced study in all the sciences applied in his work ; difficulty in seeing how they are essential to a proper understanding of the results of others' researches sometimes puts him in danger of never gaining an interest in the fundamental principles of science.

This book contains the result of many years' experience in the endeavour to show the student how even the most fundamental facts and inferences of Chemistry and Physics have at once a bearing on his practical work and observations. The inductive methods generally used are not different from those of farmers and practical men who by comparison of their results draw inferences as to the effects produced in their field work and then proceed to apply them. The more advanced work based on chemical and physical principles deduced from mathematical considerations has been left for specialist study.

The author hopes that the book will be found useful, and acknowledges the friendly influence of Professor T. B. Wood during the course of many years of collaboration.

R. H. ADIE.

CAMBRIDGE,
October, 1926.

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CHEMISTRY FOR AGRICULTURAL STUDENTS.

CHAPTER I.

INTRODUCTORY.

1. The Scope of Chemistry.—Chemistry is the science which is most directly concerned with changes in the properties of objects which surround us. By properties we mean characters which are evident to our senses, such as colour, smell, taste, hardness, heaviness, etc., classed as *physical properties*, and those which are shown when a body is placed in contact with another body or when it is heated by itself or with other bodies, classed as *chemical properties*. Chemistry further tries to explain the existence of these properties and why each body acts in the way it does.

Our knowledge of properties has been slowly accumulating through centuries, but it is only since the beginning of the nineteenth century that any satisfactory theory has been suggested to account for the facts. Since that date chemistry has continually advanced, the advance becoming more rapid with the passage of time, until an enormous mass of material, both practical and theoretical, is now available. A large amount of this material has a direct bearing on agriculture. Much has served its purpose and been superseded by more exact knowledge, and the student of agriculture must always be prepared to follow the most recent advances if he is to take advantage of the research work carried out on his behalf.

So wide, however, is the subject that we must in this book keep as far as possible within the limits set by the direct study of plants and animals and their products, while attempting as far as may be to outline the accepted explanations of the changes which we meet.

2. The Action of Heat on Grass.—We may begin the study of the chemical properties of plants by a very simple experiment.

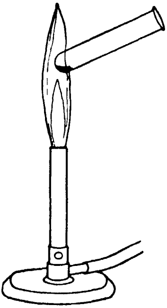

Fig. 1.

Exp. 1.—Take a dry test-tube and in it place a few blades of grass or pieces of other green leaves. Shake the grass or leaves down the tube and hold the tube in a nearly horizontal position over a flame, but do not heat more than the closed end (Fig. 1). Continue heating carefully.

We first notice that the grass gradually turns brown and that a mist appears, which settles in small drops on the colder part of the tube. The appearance of the mist and drops of liquid, together with the known drying of grass to form hay, suggests that the liquid may be water, but in chemical work it is essential that we should verify each inference, if possible, by some conclusive test. We can confirm the identity of water by examining its boiling and freezing points, but a simpler chemical method will be sufficient.

Exp. 2.—Powder a small quantity (about ½ teaspoonful) of blue vitriol (also known as bluestone, or copper sulphate crystals) and heat the powder gently over a small flame in a tin pan or porcelain crucible, until its colour turns to white. Now take several watch glasses and put into different ones a few drops of (*a*) water, (*b*) pure alcohol, (*c*) paraffin oil, (*d*) turpentine, (*e*) benzene, (*f*) the liquid from the grass, and drop into each liquid a small quantity of the colourless copper sulphate.

We note that the colourless solid turns blue again in contact with water and also with the liquid from the grass, but that it is not changed by the other liquids, so that we may infer that the liquid (*f*) is water, until we find another common colourless liquid besides water to turn the colourless powder blue.

The colourless copper sulphate is called *anhydrous copper sulphate*, and the turning blue of anhydrous copper sulphate is a simple *test* for water.

3. **Further Effects of Heat on Grass.**—As we continue the heating (Exp. 1) we notice that less water is given off and the mist becomes yellow and finally brown; from the mist a brown liquid appears on the sides of the test tube. The fumes and liquid have a tarry smell, and may burn when a lighted taper is held at the mouth of the test tube. Drops of tar, which do not mix with the water in the tube, also appear. A black substance, which has for a long time been known as *charcoal*, is left in the bottom of the test tube.

Exp. 3.—Shake out the charcoal from the test-tube on to a piece of sheet iron, a patty pan or a crucible lid, and heat to redness.

We note that the black charcoal burns away leaving a small quantity of a fine white ash, which does not appear to change on further heating.

4. **Chemical Constituents of Vegetable Matter.**—As a result, then, of our experiments we find that a green plant when heated yields at least five different products:—

(i) water.
(ii) a gas which burns.
(iii) tar.
(iv) charcoal.
(v) ash.

Now none of these products except water can be easily connected with the air or the soil in which the plant lives, so that it will require a careful investigation of the air and the soil to discover their connection with plant life and the changes undergone by the soil and air in their conversion into plants. Before proceeding far we find that it is necessary to examine certain characters of bodies in which changes may take place without the bodies themselves becoming permanently changed, *i.e.* the physical properties mentioned in Art. 1. We can then examine the chemical properties of the bodies and try to see how the changes come about which turn air and soil into vegetable matter.

CHAPTER II.

MEASUREMENT : DENSITY : SPECIFIC GRAVITY.

5. Solids, Liquids, and Gases.—The common substances which we meet in agricultural life group themselves broadly into three classes. The first class contains those things which are firm to the touch and have a shape of their own, such as stones, corn, trees, the farm animals, implements, etc. Though these are made up of different materials *they keep their own shape* unless they are forced into other shapes by pressure, etc.; such things are called *solids.*

The second class contains those things which take the shape of any vessel into which they may be put, such as water, milk, paraffin oil, etc. These things have a visible top or surface where they are touching the air, and are called *liquids.* The surface of a liquid at rest is flat except where it touches a solid, and to this most important point we must return later.

The third class contains things which resemble those of the second class in taking the shape of any vessel in which they may be put, but they *do not form any definite surface* when allowed to stand in an open vessel. In the air they rapidly disappear, and when shut up in a vessel they gradually move about until they form a uniform mixture all over the vessel. Substances in this class are called *gases.*

Exp. 4.—Take three glass jars or cylinders and place in them respectively :—

(i) some orange jelly square melted with about an equal volume of water and allowed to set ;

(ii) some solution of potassium dichromate, matching the colour of the jelly ;

(iii) a small quantity of scraps of copper and some nitric acid. (N.B.—This part of the experiment should be done in a draught chamber, out of doors, or on the window sill.)

In each case cover the jar with a piece of glass.

The three jars will in a short time appear of a uniform orange colour, and will be hardly distinguishable, but on removing the glass plates and tilting the jars the jelly will keep its shape and refuse to be poured out, the solution will retain a surface and be easily poured out, while the orange fumes will tail off into the air and will also be easily poured out into another jar. Therefore (i) contains a solid, (ii) a liquid, and (iii) a gas.

The characteristic properties of these three classes show considerable variations. Thus some solids, like sponge, can be easily compressed, as they are full of air holes, *i.e.* they are *porous*; and others, such as indiarubber and steel springs, can be easily bent but return to their original shape when the bending force is removed—these are *elastic*; paraffin wax candles and sealing wax bend in warm weather; treacle pours with difficulty and is called *viscous*; but exceptions can be dealt with as they arise.

6. **The Metric System.**—In determining the shape or size of bodies, units of measurement have been fixed. At one time very many different units were in use in this country, but these are now reduced to standards by Act of Parliament. In practically all laboratory work throughout the world the *metric system* is used in measuring and weighing, and it is based on the three fundamental units of length, mass or weight, and time.

7. **Measures of Length.**—The standard of length in the metric system is the *metre*, which was intended to be (and is very nearly) one ten-millionth of the distance between the equator and the N. or S. pole of the earth.

The metre is subdivided as follows into tenths, hundredths, etc., Latin prefixes being employed to denote these subdivisions:—

1 metre = 10 decimetres or 10 dcm.
= 100 centimetres or 100 cm.
= 1000 millimetres or 1000 mm.

The scale in Fig. 2 is divided into centimetres and millimetres.

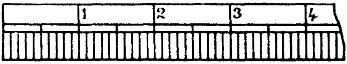

Fig. 2.

Similarly, Greek prefixes are used to indicate multiples of the metre ; thus :—

10 metres = 1 dekametre,
100 ,, = 1 hektometre,
1000 ,, = 1 kilometre.

In the British system, which is used in commerce and in engineering, the fundamental unit of length is the standard yard, of which copies have been made. It is subdivided into 3 feet and 36 inches.

The most convenient relations between the metric and British systems to recollect are :—

1 inch = 2·54 cm.,
1 metre = 39·37 in.

8. Measures of Area.—The measurement of area is not often required in chemistry. The metric measures are derived from the unit of length, so that unit area is a square with sides 1 metre long, and is called 1 *square metre.* This is subdivided thus :—

1 sq. metre = 100 sq. dcm.
= 10,000 sq. cm.
= 1,000,000 sq. mm.

The corresponding British units are the square yard, etc., and the acre of 4840 square yards.

The measures of larger areas do not concern us here, but are rather a matter for the surveyor and the engineer.

9. Measures of Volume.—The measurement of volume is of the utmost importance, and we have frequently to determine the volumes of solids, of liquids, and of gases. The metric standard of volume is derived from the metre, and would naturally be a cube with edges 1 metre long, *i.e.* a *cubic metre*, but since this volume is too large for general use, the thousandth part has been adopted as the general standard for all purposes. This unit is the volume of a cube of 1 dcm. edge, a cubic decimetre, or 1 *litre*, and is subdivided into 1000 cubic centimetres. We thus use practically only two units of volume:—

$$\tfrac{1}{1000}\text{ cub. metre} = 1\text{ litre},$$
$$1\text{ litre} = 1000\text{ cubic centimetres}$$
or
$$= 1000\text{ c.c.}$$

The standard British units of volume are the Imperial gallon, which is the volume occupied by 10 lb. of pure water at 62° F., the bushel of 8 gallons, and the quarter of 8 bushels. It is convenient to recollect that

$$1\text{ litre} = {\cdot}22(01)\text{ gallons},$$
$$1\text{ cub. ft.} = 6{\cdot}25\text{ gallons}.$$

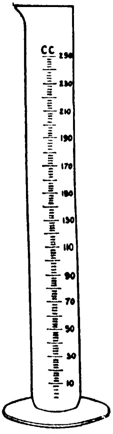

Fig. 3.

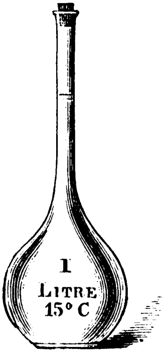

Fig. 4.

The instruments chiefly used in measuring volumes are the measuring cylinder and flask, the burette, and the pipette.

The *measuring cylinder* (Fig. 3) is a cylindrical glass jar graduated generally in c.c. throughout its length. Since it is usually wide, the length occupied by 1 c.c. is small, and great accuracy is not obtained.

Greater accuracy can be obtained by increasing the length occupied by 1 c.c., *i.e.* by diminishing the width of the tube. In measuring large volumes this would make the tube inconveniently long, so that it is usual to take a flask with a narrow neck on which a single mark is made, representing a definite volume, *e.g.* 1 litre, 500 c.c., etc. Such a flask is called a *measuring flask* (Fig. 4).

In measuring small volumes the difficulty of pouring out an accurate amount from any measure makes it more convenient to draw off the liquid by a tap or a pinchcock at the bottom of the measure. The measure used is a tube which generally holds 50 c.c. and is of such a width that 1 c.c. occupies about 1 cm. of its length ; in this way the tube can be graduated in $\frac{1}{10}$ c.c., forming easily readable divisions : it is called a *burette* (Fig. 5). The graduations generally read from above downwards.

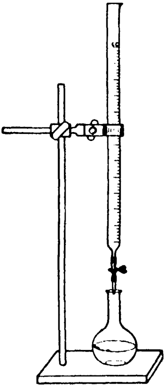
Fig. 5.

Greater accuracy is obtained by diminishing the bore of the tube still further, but in this case, in order that a reasonably short tube may hold a fair quantity of liquid, it is usual to blow a bulb in the middle and use a single graduation. This forms a *pipette* (Fig. 6). The narrow tubes (*a*) are generally about 20 cm. long, to enable liquids to be sucked from bottles, etc.

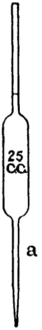

Fig. 6.

In using all these instruments it must be remembered that the eye must be placed on a level with the surface of the liquid, and the lowest point of the curved surface (*meniscus*) must appear to touch the graduation line which is being read (Fig. 7). This makes sure that all the graduations read correspond with one another : if a burette is read from above, the mark on which the meniscus falls is too high, so that the reading is too low, while if viewed from below the mark read is too low and the reading is too high (Fig. 8).

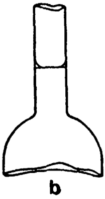

Fig. 7.

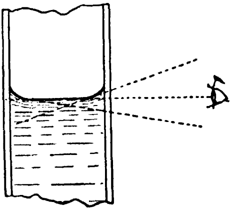
Fig. 8.

10. Measures of Mass and Weight.—The accurate measurement of the quantity of matter in any body, correctly called the *mass* of the body, is of fundamental importance in chemistry. The metric standard of mass is derived from the unit of volume and is intended to be the mass of 1 c.c. of pure water at 4° C. : this unit mass is called a *gramme*, or generally in chemistry a *gram*. A gram is too small for practical use as a standard, so that the actual standard is the mass of a lump of platinum which was made to represent the weight of 1000 c.c. or 1 litre of pure water at 4° C. as nearly as possible, and the gram is actually $\frac{1}{1000}$ of the weight of this standard "kilogram." The gram (like the metre) is subdivided into tenths, hundredths, etc., and multiplied by tens, thus :—

1 gram or 1 gm. = 10 decigrams or 10 dcg.
= 100 centigrams or 100 cg.
= 1000 milligrams or 1000 mg.,
10 gm. = 1 dekagram,
100 gm. = 1 hektogram,
1000 gm. = 1 kilogram.

The British standard of mass resembles the corresponding standard of length in being the mass of a lump of platinum of which copies are made. The commercial standards derived from the pound are the hundredweight of 112 lb., the ton of 2240 lb., and the cental of 100 lb.

It is convenient to recollect that

1 gram = 15·43 grains,
1 kilogram = 2·2(05) lb.
1 lb. = 454 grams.

In chemistry we nearly always compare masses by the balance, and the distinction between weight and mass has little importance; the terms are generally used as interchangeable.

We require, for weighing, a balance which shows differences of weight of 1 cg. between loads of 50 gm. in each pan. Greater accuracy in weighing can easily be obtained, but the beginner's errors of experiment will generally prevent any greater accuracy being derived from the more accurate weighing. A set of accurate weights is, however, of importance, especially those which run from 10 gm. downwards.

The balance in general use has a brass beam and three agate or steel knife edges, the two side edges being at equal distances from the centre one, and all three in a straight line. The beam rests on the middle knife edge, which stands upon two plates of agate or steel, while the scale pans are suspended from the end knife edges by stirrups of the same materials. A long pointer with its end over a scale is fixed to the middle of the beam and a movable weight to one end* (Fig. 9).

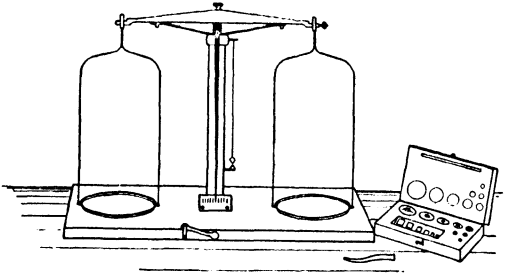

Fig. 9.

In chemical work, weights of substances are nearly always determined by difference, so that the substances are not weighed upon the pans, but in or upon some vessel : for example, the weight of a quantity of liquid or solid is obtained by weighing the substance in some vessel and then subtracting the weight of the vessel. The principal vessels in use are the watch glass, weighing tube or bottle, U-tube, crucible, and in the case of gases, a glass globe of about 250 c.c. capacity.

11. The Measurement of Density.—The *density* of any substance is the ratio of its mass (weight) to the volume it occupies; in the metric system it is usually stated in grams per c.c.

---

* In the absence of a fixed balance good results can be obtained by the use of a pair of photographic scales with a good set of weights.

Since the density of any substance is obtained by dividing its weight by its volume, the determination of density involves two measurements, one of weight and the other of volume.

12. To Find the Density of a Solid.—In the case of a regular solid such as a rectangular block of wood or metal the dimensions of the solid can be measured, and the volume in cubic centimetres calculated from these. The density is then obtained by dividing the weight, measured in grams, by the calculated volume. When the solid is irregular in shape, *e.g.* a stone, we may proceed as in the following experiment.

Exp. 5.—Take a stone and weigh it. Take a graduated measuring cylinder into which the stone will just slip and half fill it with water, adjust the water level so that it just reaches one of the marks, and read the level. Now slip the stone gently into the inclined cylinder and shake off any air bubbles, stand the cylinder upright and read the second level. The difference between the two readings represents the water displaced by the stone, and therefore the volume of the substance of the stone. Divide the weight by the volume and obtain the density.

Enter your results thus:—

Weight of stone ... ... = 28 gm.
Second level of water in measuring glass ... = 62 c.c.
First ,, ,, ,, ,, = 50 c.c.
Volume of water displaced = volume of stone = 12 c.c.

Hence density of stone = $\frac{28}{12}$ = 2·3 gm. per c.c.

A solid which is in the form of a powder, *e.g.* soil, should be first weighed on a piece of paper or a watch glass, then tipped carefully into the cylinder and its volume measured as in Exp. 5. In the case of a soluble solid, *e.g.* sugar, we can use in the cylinder (*a*) a liquid in which the solid is not soluble, or (*b*) a saturated solution of the solid in water.

13. To Find the Density of a Solid by Means of a Density Bottle.—When a solid is in small fragments or in a powder the volume is accurately found by displacement of water in a *density bottle* (*specific gravity bottle*), which is a small bottle fitted with a glass stopper through which a hole is bored (Fig. 10).

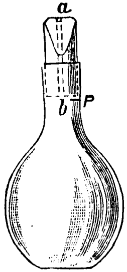

Fig. 10.

Exp. 6.—Take a specific gravity bottle, fill it with distilled water, replace the stopper, making sure that no air bubbles are left, wipe, and weigh. Weigh out about 10 gm. of dry soil or sand, pour some of the water from the bottle, dry the neck, put in the soil or sand, and refill with water; shake out air bubbles, replace the stopper, and wipe and weigh again.

Enter your results thus : –

Weight of bottle full of water = 32·40 gm.
Weight of sand ... ... = 10·04 gm.
[Add.] 42·44 gm.
Weight of bottle with water and sand inside ... ... = 38·42 gm.
[Subtract.] Loss of weight = 4·02 gm.

Now this loss of weight must be the weight of the volume of water displaced by the sand, and since 1 gm. of water occupies 1 c.c.,

Loss of weight in grams = volume of sand in c.c. = 4·02 c.c.

$$\text{Density of sand} = \frac{\text{weight}}{\text{volume}} \text{ gm. per c.c.}$$

$$= \frac{10{\cdot}04}{4{\cdot}02} = 2{\cdot}50 \text{ gm. per c.c.}$$

14. To Find the Density of a Liquid, *e.g.* **Milk.**—In the case of liquids two methods are possible :—(i) find the weight of a known volume, (ii) find the volume of a known weight. The former is most generally used, and two methods of carrying out the determination are indicated in Experiments 7 and 8.

Exp. 7.—Weigh a small beaker, measure 20 c.c. of milk by means of a pipette into the beaker and weigh again. Calculate the density. In this case the milk surface must be accurately adjusted so that the lower side of the curved surface (*meniscus*) touches the volume line marked on the neck of the pipette, and when the pipette has drained for a few seconds the bulb must be warmed with one hand while the finger is placed on the open top; this expels the last drop required to make the volume of the milk equal to that marked on the pipette.

Greater accuracy is obtained if a narrower tube can be used for the volume mark. A density (specific gravity) bottle has a very narrow tube through the stopper, and is very accurate.

Exp. 8.—Take a dry density bottle and weigh it, fill it with milk, put in the stopper, avoiding air bubbles, and dry the outside very carefully, handling it as little as possible with the naked hand. Weigh it again. In order to find the volume rinse the bottle well with water, fill it with distilled water, dry it as before, and weigh it.

Enter your results thus:—

Weight of density bottle full of milk	= 68·35 gm.
,, ,, ,, empty	= 16·91 gm.
Weight of milk	= 51·44 gm.
Weight of density bottle full of water	= 66·86 gm.
,, ,, ,, empty	= 16·91 gm.
Weight of water	= 49·95 gm.

Now 1 gm. of water occupies 1 c.c., so that the volume in c.c. of the water, the bottle, and the milk respectively = 49·95 c.c. Hence density of milk $= \frac{51 \cdot 44}{49 \cdot 95} = 1 \cdot 03$ gm. per c.c.

15. Apparent Density.—Agricultural produce is generally sold by volume, controlled by weight, *e.g.* the Imperial quarter or 8 bushels of wheat weighing 480 lb., so that the standard density of wheat is 60 lb. per bushel. This result, obtained by calculating the relation between weight and volume of a grained or powdered substance, which does not take into account the spaces between the particles, is called the *apparent density*.

Exp. 9.—Weigh out 100 gm. of corn, or dry soil or sand, and pour it into a dry measuring cylinder. Read the volume of the solid.

Thus if 100 gm. of a dry soil occupy 63·5 c.c., then :—

$$\text{Apparent density of soil} = \frac{\text{weight}}{\text{volume}}\ \text{gm. per c.c.}$$

$$= \frac{100}{63{\cdot}5} = 1{\cdot}57\ \text{gm. per c.c.}$$

Greater accuracy can be obtained by the method of Exp. 10.

Exp. 10.—Take a small glass measuring flask and fill it to the mark with the corn, or dry soil or sand, tapping the flask gently before making the last adjustment. Weigh the flask and solid again, and find the weight of the solid.

Enter your results thus :—

Weight of flask and soil = 185·48 gm.
,, flask = 27·40 gm.

Weight of soil = 158·08 gm.
Volume of flask = 100 c.c.

Then apparent density of soil

$$= \frac{158{\cdot}08}{100}\ \text{gm. per c.c.} = 1{\cdot}58\ \text{gm. per c.c.}$$

16. Air Space in Soils.—The apparent density of a soil is always less than its true density, and the difference must be due to the air spaces between the particles of the soil. The relative values of the true and apparent densities can be made to give us valuable information about the amount of air space and the condition of the soil. Thus if the apparent density of a soil is 1·58 gm. per c.c. and its real density 2·50 gm. per c.c., the volume actually occupied by 1 gm. of true soil $= \frac{1}{2{\cdot}50}$ c.c., and the volume occupied by 1·58 gm. of true soil $= \frac{1{\cdot}58}{2{\cdot}50}$ c.c. = ·632 c.c.

Now since there are 1·58 gm. of true soil in 1 c.c., the volume occupied by the true soil must be ·632 c.c., and the air space in 1 c.c. = 1 — ·632 c.c. = ·368 c.c.

That is, the volume of the air space is 36·8 per cent. of the total volume.

It may be noted that values for the air space thus obtained do not make any special allowance for the presence of water in the soil, either as such or in combination with soil constituents, and that the amount of air space will vary to some extent with the amount of shaking of the soil before measuring, causing better packing.

Apparent densities are used in checking the packing of substances sold by measure; thus the standard imperial bushel of wheat should weigh 60 lb., and that of potatoes 56 lb.

17. Specific Gravity.—The numbers which are found for the densities of bodies are expressed in the units of weight and volume, and can be almost as easily determined in the British system as in the metric. They have, however, the disadvantage of being different for the same substance according to the units selected. Thus a body of density 2·5 gm. per c.c. has also a density of 25 lb. per gal., 156 lb. per cub. ft., and 1·8 tons per cub. yard.

A method of avoiding this difficulty was early adopted by scientists in expressing the relative densities of all solids and liquids in terms of water = 1, and of all gases in terms of air = 1; that is to say, the densities of all substances were expressed as the ratio of the weight of any substance to the weight of an equal volume of water (or air). The numbers obtained in this way are called *specific gravities*, and are practically the same in value as the densities of the same substances expressed in gm. per c.c.

Thus we can, for example, use the results obtained in Exps. 5 and 8 respectively, for determining the specific gravity of a solid and of a liquid.

In Exp. 5, if 28 gm. of stone occupy 12 c.c. and 1 c.c. of water weighs 1 gm.

Then specific gravity of stone

$$= \frac{\text{Weight of stone}}{\text{Weight of equal volume of water}}$$

$$= \frac{28}{12 \times 1} = \frac{28}{12} = 2{\cdot}3.$$

Also in Exp. 8, if :—

Weight of milk filling density bottle = 51·44 gm.
and „ water „ „ „ = 49·95 gm.

Then specific gravity of milk

$$= \frac{\text{Weight of milk}}{\text{Weight of equal volume of water}}$$

$$= \frac{51{\cdot}44}{49{\cdot}95} = 1{\cdot}03.$$

18. The Principle of Archimedes.—In the determination of specific gravities another principle which is found to be of great use is based on the fact that when bodies are placed in a liquid they appear to lose some or all of their weight. The principle states that when a body is immersed in a liquid the loss of weight is equal to the weight of the volume of liquid displaced; this is known as the *Principle of Archimedes*, and the results are immediately available for determining specific gravities.

Thus if a solid weighs 28 gm. in air and is then suspended in water and found to appear to weigh only 16 gm., the loss of weight (= 28 − 16 = 12 gm.) is the weight of the volume of water displaced, *i.e.* the weight of a quantity of water of the same volume as the solid.

Hence specific gravity of the solid

$$= \frac{\text{Weight of solid in air}}{\text{Weight of equal volume of water}}$$

$$= \frac{\text{Weight in air}}{\text{Loss of weight in water}}.$$

19. The Hydrometer and Lactometer.—The principle of Archimedes also applies to solids floating in a liquid, which sink no further when the weight of the volume of liquid displaced has become equal to the weight of the solid.

Exp. 11.—Take a long thin-walled glass tube, *e.g.* a long test-tube, and weight it with shot until it floats in water in a vertical position. Measure the length of tube projecting above the surface of the water and the whole length of the tube (allowing for the rounded end if necessary); the difference is the length of tube immersed. Repeat, using milk, spirit, and strong brine, and compare the results.

We know that the density of each liquid

$$= \frac{\text{Weight of volume of liquid displaced}}{\text{Volume of liquid displaced}}.$$

Whence

$$\text{Weight of volume of liquid displaced} \\ = \text{Volume of liquid displaced} \times \text{Density of liquid.}$$

For the water,

$$\text{Weight of volume of water displaced} \\ = \text{Volume of water displaced} \times \text{Density of water.}$$

Now the weights of the volumes of liquid and water displaced are both equal to the weight of the tube, hence :—

$$\text{Volume of liquid displaced} \times \text{Density of liquid} \\ = \text{,, water ,,} \times \text{,, water,}$$

or
$$\frac{\text{Density of liquid}}{\text{Density of water}} = \frac{\text{Volume of water displaced}}{\text{Volume of liquid displaced}}.$$

If the tube is of uniform cross section then the volume of liquid or water displaced = area of cross section × length immersed,

and
$$\frac{\text{Density of liquid}}{\text{Density of water}} = \frac{\text{Length immersed in water}}{\text{Length immersed in liquid}}.$$

But we take the density of water to be 1, so that

$$\text{Density of liquid} = \frac{\text{Length immersed in water}}{\text{Length immersed in liquid}}.$$

Such a tube can be graduated to show a range of densities and can then be used for rapid determinations of densities of liquids. For accurate work the tube would be inconveniently long, and it can either be coiled up or, more generally, blown into a bulb displacing a volume equal to that of a known length of the tube, when the position of the graduations can be calculated from the water standard. Such an instrument is called a *hydrometer* (Fig. 11), and is graduated to read the densities of liquids heavier or lighter than water.

If the bulb is large and the tube small the readings may be very delicate, as in the case of the *lactometer*, which can be used for rapidly checking the density of milk.

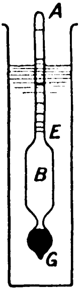

Fig. 11.

20. Hare's Method of Comparing Densities of Liquids.—Hare's method of comparing the densities of two liquids requires no expensive apparatus and is capable of considerable accuracy, so that it is suitable for use in a farm dairy for rapidly determining the density of milk. The method is based on the fact that when air is partly sucked out from two vertical tubes connected at the top and standing in two liquids, the liquids rise to heights which are inversely proportional to their densities. The amount of suction must be the same in both tubes, and they must have the same diameter unless their bore is over ¾ inch.

Exp. 12.—Take a long piece of glass tube and halve it so that the pieces are each about 1 metre long. Make or take a T piece of glass or brass tube and connect it with the two tubes by india-rubber tubing as in Fig. 12. Attach a longer piece of india-rubber tube with a pinchcock to the third limb of the T piece. Now take two beakers or tumblers and put milk into one and distilled or soft water into the other; place one tube in each liquid, support the tubes upright, and suck air from the top until the tubes are nearly full. Measure the height of each column of liquid, h_1 and h_2, above the surface in its beaker.

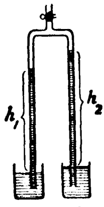

Fig. 12.

Since the heights of the columns are inversely proportional to their densities,

$$h_1 d_1 = h_2 d_2,$$

where d_1 and d_2 are the densities of the liquids of which the heights of the columns are h_1 and h_2 respectively. Thus, if the column of water had a height of 652 mm., and that of milk had a height of 632 mm.,

$$652 \times 1 = 632 \times d_2,$$

$$\text{or } d_2 = \frac{652}{632} = 1{\cdot}032 \text{ gm. per c.c.}$$

The law can be easily verified by using liquids of known density to start with.

21. The Density of Gases is generally determined by *Dumas' method*, which resembles the specific gravity bottle method, except that the volumes weighed are large. Examples will be worked later (see Exp. 37). The method of determining the volume of a known weight is very generally used in cases of liquids whose density in a state of vapour is required: it is called *Victor Meyer's method.*

22. The Measurement of Time.—In the metric system the general method of dividing time into years, days, hours, minutes, and seconds has been retained.

CHAPTER III.

AIR: OXYGEN: NITROGEN.

23. Reasons for Studying the Air.—We have already noted in our first experiment (Exp. 1, p. 2) that plants contain a number of different substances. We also know that a single seed of corn or of another plant yields many seeds of the same kind during its life, in addition to its stem, leaves, and roots, so that it must be able to obtain the substances required for the increase of weight, *i.e.* plant food, from some source.

As far as we can observe the only possible sources of plant food which the plant can get at during its life are the soil and the air. Since a plant can only grow in moist soil and not in dry soil, we must include water in the soil source.

Now water may be salt or fresh, hard or soft, rain, river, or spring water, and we recognise at once that there are differences between these sorts of water, though they all come originally from rain water. The soils, too, in which plants grow, show still greater differences, which are enough to make it worth while to examine them carefully.

The open air, however, seems to be much the same in all places, and is always being mixed by wind, etc., so we may examine it first. The discovery of the composition of the air was very slow, so that it is worth while to go through the steps rather carefully.

24. The Examination of Air.

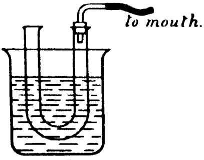

Fig. 13.

Exp. 13.—Take a piece of glass tube of about 5 mm. bore and bend it into the shape of a **U**, or take a small, thin-walled **U**-tube, and fit one end with a cork and tube bent at right angles. Put the **U**-tube into a beaker, fill the beaker with a freezing mixture, made either by mixing salt and pounded ice or by dissolving sal-ammoniac in water. By means of a piece of indiarubber tubing suck air through the **U**-tube (Fig. 13). Take out the tube and examine it from time to time. Note your observations.

Exp. 14.—Put small pieces of quicklime into a bottle until it is about one quarter full; fill the bottle with water, cork it, shake well, and allow it to stand till the liquid is clear; pour off the clear liquor, *which is called lime-water*, into another bottle and cork tightly. Pour some lime-water into a test-tube or small beaker and blow air through it by an india-rubber scent-bottle bellows, or by a pair of bellows attached to a piece of glass tube by means of a short piece of indiarubber tube (Fig. 14). Note whether any change is seen and the time taken for your observation.

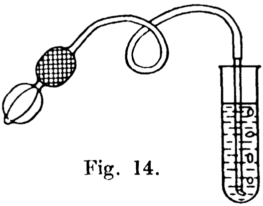

Fig. 14.

We note that the air contains water, and since clear lime-water already contains water, something which slowly turns lime-water milky must be present in the air. Now we must make it a fundamental principle to experiment only with pure substances, so that it becomes necessary to remove the other substances from the air as impurities.

25. **The Purification of Air.**—We may have noticed that quicklime takes up water which is poured upon it and so becomes slaked.

Exp. 15.—Weigh a lump of quicklime, put it on a plate, and pour on it about $\frac{1}{8}$ of its weight of water. Note what takes place. Weigh again when cool.

We note that the quicklime becomes hot, and after a time leaves a dry powder which weighs more than the original quicklime, so that the water seems to have joined itself to or become part of the solid. We might, therefore, find out if quicklime has any effect upon the water in the air, and also upon the substance which turns lime-water milky.

Exp. 16.—Take a piece of glass tube about 30 cm. long and 2 cm. bore. Fit it with two corks, each bored with a single hole through which passes a short, straight piece of glass tube. Fill this tube with lumps of quicklime and attach one end to the clean **U**-tube used in Exp. 13, by means of a piece of indiarubber tube (and a cork, etc., if required), using the freezing mixture as before (Fig. 15). Suck air through and note the result.

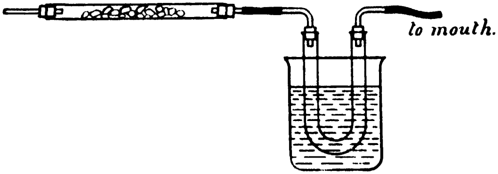

Fig. 15.

Exp. 17.—Attach the tube of the bellows to one end of the tube of lime prepared in the last Exp., and a straight tube to the other end. Blow air through the lime into lime-water contained in a test-tube as in Exp. 14. Note the result.

We observe that air which has passed over quicklime has lost both water and the substance which turns lime-water milky. No other impurities can be easily discovered, so that we say that air which has been passed over quicklime is *pure*.

26. The Composition of Air.

Exp. 18.—Wind a piece of thin wire round a short candle and bend it so that the candle can be lowered alight into a gas jar; also take a deflagrating spoon without its cover and place in it a small piece (about the size of a split pea) of dry phosphorus.* Light both the candle and the phosphorus (the latter by warming it) and lower them into two gas jars (Fig. 16). Note what takes place.

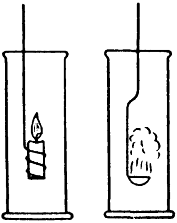

Fig. 16.

Both candle and phosphorus continue to burn and only go out when they have burnt completely.

Exp. 19.—Repeat Exp. 18, but place sheets of cardboard or deflagrating spoon covers over the gas jars. When the contents of the cylinders are clear, test them by plunging a lighted taper into each. Note your observations.

Since both candle and phosphorus go out, they may have burned away as before, but we note that most of the candle is left, while the phosphorus lights again when brought into the air. Also, since the lighted taper is extinguished in the gas jars in both cases, it appears that the air in which either a candle or phosphorus has burnt has been changed by the burning.

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* Phosphorus is dangerous to handle, and beginners must be careful to touch it only with a pair of tongs. It may be cut *under water* in a shallow dish, and each piece may be dried as wanted by rolling it on a dry piece of blotting-paper.

We can now ask two questions : (i) Is the air changed in the burning by the addition of something which puts a taper out, or (ii) is the air changed by the loss of something which will make a taper burn ? To investigate this point we must choose a method of shutting up our gas jar of air which will not prevent us from seeing any changes of volume.

Exp. 20.—Take two bell jars about 20 cm. in diameter, fit them with tightly fitting corks, and stand them in basins in water about 5 cm. deep, marking the level of the water (with the corks removed) by means of a strip of gummed paper. Take two thin, broad corks ; place on one of them a small lighted candle and on the other a small dish or crucible containing a small piece of dry phosphorus. Float the corks in the dishes and over them place the uncorked bell jars. Cork the jar with the lighted candle at once, light the phosphorus by dropping a little hot sand on it (or by touching it with a hot wire), and cork the jar quickly (Fig. 17). When the flames have gone out, allow the jars to cool and mark the level of the water inside them by means of gummed paper. Note what has taken place. Roughly measure the original and final amounts of air in the bell jars by measuring the distances from the two levels of water to the shoulders of the jars.

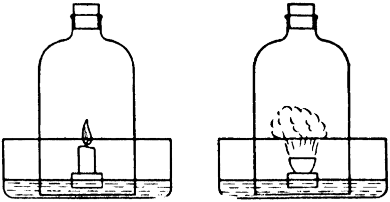

Fig. 17.

From this experiment we note that some of the air disappears when things burn in it, and that the amount which disappears is about the same fraction of the whole in the two cases observed.

In order to find out if it is really the loss of some substance that has caused the air to lose its property of making things burn, we must trace the lost material, and we might hope to obtain the lost air for examination from the burnt phosphorus.

Exp. 21.—Put a small piece of dry phosphorus under a dry bell jar standing on a dry plate. Light it with a hot wire and replace the bell jar. As soon as the fumes have settled collect them and put them in a test-tube. Heat them and note any change.

Since no change can be observed, the phosphorus cannot help us further at present, so we must use something else; metals are common, and may be useful for this purpose.

Exp. 22.—Heat a short piece of magnesium ribbon in a flame. Drop some iron filings and also some precipitated copper through a flame. Note their behaviour.

Since metals burn in air when made hot, we may now use this burning to help our research.

***Exp. 23.**—(*Demonstration Exp.*) Take a round-bottomed flask (Florence flask) or boiling tube, and in it place 4 or 5 strips of bright copper foil. Draw off the neck to a fine tube and allow it to cool. When cool seal the fine tube by a flame, leaving a point. Take a small cast-iron saucepan, put into it the flask or tube, and cover this with sand. Place the saucepan over a gas burner and heat it for at least 24 hours. When cold examine the tube. Place the neck under water and break off the point. Note any volume changes; break off the neck and put in a lighted taper. Note the effects.

When copper is heated in a closed flask of air it turns black; when the tip of the flask is broken under water, the water rushes in and the gas which is left in the flask puts out a burning taper. Hence we notice the same two facts as in the cases of the burning candle and phosphorus—(i) the air in which a substance has burnt puts out a burning taper, (ii) some of the air seems to disappear.

Note.—The fraction of air which has been used up by the copper may be determined by weighing (a) the flask and water sucked in, then shaking out the water and weighing (b) the empty flask and copper, and lastly filling the flask full of water and weighing again (c). The fraction $\frac{a-b}{c-b}$ represents the fraction of air lost.

Exp. 24.—Take a piece of hard glass tube of about 1 cm. bore and 65 cm. long, bent in the middle at an angle of about 120°. Into one of the limbs put a roll of copper gauze or some strips of copper. Now weigh the tube. Fix the tube in a clamp with the empty limb horizontal (Fig. 18) and heat the copper. When cool weigh again and compare with the former weight.

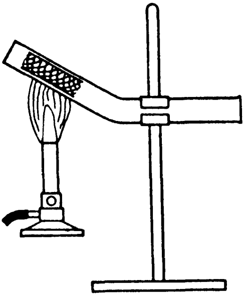

Fig. 18.

Since the copper increases in weight when heated in air, we note that the disappearance of air is accompanied by an increase of weight in the burning (changing) substance.

Exp. 25.—Collect some of the black burnt copper from Exp. 24, put it in a hard glass tube, and heat it. Now light a thin strip of pine wood or a match stalk and blow it out, leaving a glowing tip; lower the glowing end into the tube and note the result.

No change can be observed either in the burnt copper or in the air of the tube, showing that we are still unable to find the substance lost from the air.

***Exp.** 26.—(*Demonstration Exp.*) Repeat Exp. 23, placing a few c.c. of mercury in the flask instead of the copper, and keeping the flask heated in the sand bath until it is well coated inside with a red powder, *red precipitate*. Break the end of the flask (or tube) under water as before and test the gas left with a lighted taper.

We again note the same facts as we have observed in the cases of copper, phosphorus, and a candle, viz. that when these substances are heated in air some of the air seems to disappear and that the air which is left puts out a burning taper. This suggests that the process of burning must be the same in all four cases, and that inferences drawn from any one case will apply to all.

Exp. 27.—Break the flask (or tube) used in Exp. 26 and scrape the red precipitate off the glass; dry it on blotting-paper; place it† in a small hard glass test-tube and heat it. Note what takes place and test the contents of the tube with a glowing splint as in Exp. 25.

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† For class purposes the teacher will provide commercial red precipitate.

We observe that the red precipitate turns brown, then nearly black, and a grey metallic ring appears inside the tube : the glowing spark also brightens and bursts into flame.

From this experiment it would appear that we can obtain a substance from the air which makes things burn and which is removed from the air by burning substances; hence we infer that the air contains two different substances : (i) one which is removed by burning bodies, (ii) one which is left after the bodies have burnt and which puts out a burning taper; the former can be regained from burnt mercury by heating the red precipitate.

In order to test whether this inference based on our *analysis* (or splitting up) of the air is correct we must try to form air again out of these two substances, *i.e.* we must try to confirm our analysis by a *synthesis* of the original air.

Exp. 28.—Take a small bell jar of air treated as in Exp. 20 with burning phosphorus. Add to it the air or gas prepared by heating red precipitate in a test-tube fitted with a cork and glass tube bent twice nearly at right angles (a *delivery tube*) as in Fig. 19, until the air again fills the bell jar to its original mark on the gummed paper. Shake the bell jar as far as you can without allowing the air to escape. Test it with a glowing splint and a burning taper.

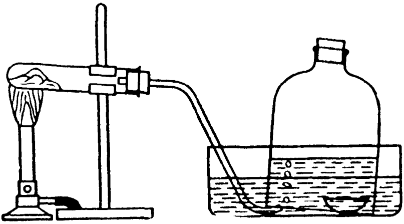

Fig. 19.

The splint goes on glowing feebly and the taper burns as in air, showing that the air we have made behaves like ordinary air. Thus our results are confirmed by synthesis.

It will be convenient, therefore, to name the two constituents we have found. The constituent (i) which is removed by burning and regained from red precipitate is called *oxygen,* while that which is left when things have burned (ii) is called *nitrogen.*

The process of burning, or joining, with oxygen is called *oxidation,* and is an example of a *chemical combination* ; the burnt substances which contain the oxygen are called *oxides, e.g.* oxide of phosphorus, black oxide of copper, red oxide of mercury ; while the separation of the red oxide of mercury into mercury and oxygen (two unlike substances) is a *decomposition.*

27. The Preparation of Oxygen.

Exp. 29.—Take five small hard glass test-tubes and heat in them (i) red lead, (ii) barium peroxide, (iii) saltpetre, (iv) potassium chlorate, and (v) potassium chlorate mixed with a little manganese dioxide. Observe any changes in the solids and test with a glowing splint to find out if oxygen is given off. Compare the readiness with which reactions occur.

In order to prepare oxygen for further examination we select the method which gives us the gas most easily, provided there are no practical objections to it.

Exp. 30.—Fit a round-bottomed or "Florence" flask with a cork and fairly wide delivery tube, bent twice nearly at right angles so that we can pass the gas into water and collect the bubbles as they rise. Into the flask put about 20 gm. of potassium chlorate mixed with about 5 gm. of black manganese dioxide. Fix the flask in the clamp of a retort stand in such a position that the end of the delivery tube passes through the side opening of a beehive shelf, or, more simply, between two small tiles, standing in a basin of water or a pneumatic trough (Fig. 20).

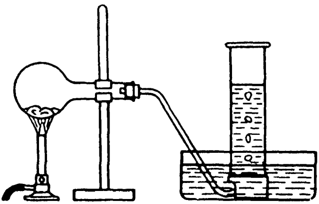

Fig. 20.

Fill a gas jar with water and put a glass plate on the top. Turn the jar upside down, stand it in the basin, remove the plate, and slide the jar over the beehive shelf or tiles, taking care that no air enters it. Carefully warm the mixture in the flask and watch the bubbles of gas given off as they rise in the jar. If the oxygen comes off very quickly turn the gas flame down a little or take away the burner for a short time. When the jar is full of gas, slide it off the beehive shelf or tiles on to the glass plate and remove it from the basin. Fill six jars in this way, remove the end of the delivery tube from the water, and then remove the flame.

Note.—It is best to reject the first jar of gas collected, which contains the air expelled from the flask, and fill it again, unless the flask is very small.

28. The Properties of Oxygen.

Exp. 31.—Take the six cylinders of oxygen prepared above and examine them as follows :—(i) Look at the gas, remove the lid and smell the gas, put in a glowing splint, leave the lid off, and test with a glowing splint at intervals of 1 minute. (ii) Place a small piece of phosphorus on a deflagrating spoon, light it, and lower it into the second jar. (iii) and (iv) Put pieces of sulphur and charcoal on deflagrating spoons, light them, and lower them into the third and fourth jars respectively. Test the products of the burning of sulphur, charcoal, and phosphorus by pouring a little litmus solution into the jars. (v) Remove the lid a moment, put in a spoonful of sand, and replace the lid. Take a small bundle of 5 or 6 strands of fine iron wire, and wind some cotton wool dipped in sulphur round one end. Light the sulphur and place the wire in the fifth jar. If the wire does not catch fire, wind more cotton wool and sulphur round and repeat. (vi) Fit a test-tube with a cork and delivery tube, and in it place some copper and some nitric acid mixed with an equal volume of water. Allow the gas which comes off to bubble into the sixth jar of oxygen standing on the beehive shelf in water. Note the results.

The properties of oxygen may be classed under two heads, (i) what it is like and (ii) what it does; the former are *physical* properties, the latter *chemical.* Under the first head come colour, taste, smell, weight, and solubility, while under the second comes the behaviour of the substance towards other substances or reagents.

Thus oxygen is a colourless, tasteless, scentless gas, rather heavier than air ; it makes burning substances burn more brightly, *i.e.* it supports combustion, and it gives brown fumes, *nitrous fumes*, when mixed with a gas given off by the action of copper and fairly strong nitric acid (the gas is called *nitric oxide*). The products of burning also generally change the colour of litmus, in the above cases turning it red.

The formation of brown nitrous fumes when nitric oxide is mixed with a gas is a proof that oxygen is present, and so is used as a *test* for that gas.

29. The Preparation and Properties of Nitrogen.—We have already, in Exp. 20, prepared nitrogen by the removal of oxygen from the air, but we have not examined its properties.

Exp. 32.—Repeat Exp. 20, burning phosphorus in a bell jar of air standing over water. Transfer the bell jar to a tub of water and turn it slowly over so that bubbles of gas rise from its lower end. Collect four jars of this gas by filling them with water in the tub, turning them upside down, holding them over the bubbles rising through the water, and covering them with glass plates as in Exp. 30. (i) Examine one jar, remove the cover, and smell the gas. Leave the cover off and test the gas every minute with a lighted taper. (ii) Light a small piece of dry phosphorus in a deflagrating spoon and lower it into the gas. (iii) Turn the cylinder upside down, keeping the cover on, slide the cover to one side until all water runs out, stand the cylinder right way up, and add litmus. (iv) Repeat (iii), but use lime-water instead of litmus. Note your results.

Nitrogen is shown to be a colourless, tasteless, scentless gas, slightly lighter than air, which puts out burning substances. It has no action on litmus, nor on lime-water.

30. The Composition of the Air by Volume.—We may now determine the proportion of nitrogen to oxygen in the air, *i.e.* the composition of the air by volume.

(*a*) Exp. 20 may be performed in such a way as to give fairly accurate results as follows :—

Exp. 33.—Take the uncorked bell jar and place it in a basin or glass crystallising pan containing water to a depth of 5 or 6 cm. Carefully mark the level of the water by means of gummed paper. Now remove the bell jar and float the crucible on the cork, putting a piece of dry phosphorus of about the size of a pea into it. Replace the bell jar, light the phosphorus by hot sand or wire, and insert the cork tightly. Hold down the bell jar so that no bubbles escape, and when the gas has cooled pour water into the dish until the water level is the same outside and in ;

mark the level again. Remove the bell jar, turn it upside down, and fill it to the second mark by water from a measuring jar; then fill it to the first mark.

The volume contained between the marks indicates the proportion of oxygen contained in the original volume of air taken.

Thus, for example :—

Volume of water required to fill bell jar to first mark	= 1275 c.c.
Volume of water required to fill bell jar to second mark	= 1020 c.c.
Difference = volume of oxygen used up	= 255 c.c.

Thus 1275 c.c. of air contain 255 c.c. of oxygen, and 100 c.c. of air contain $\frac{255 \times 100}{1275}$ c.c. = 20 c.c.

(*b*) Oxygen can be absorbed by liquids as well as by solids.

Exp. 34.—Take a solution of caustic potash or soda in a test-tube and into it drop a pinch of pyrogallic acid. Note the result.

We observe that the mixture turns brown, but that it is more coloured at the surface where it touches the air. We may try the effect of mixing these substances in absence of air.

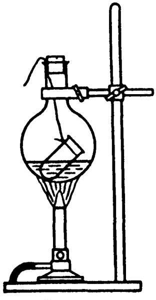

Fig. 21.

Exp. 35.—Take a small (150 c.c.) round-bottomed flask and fit it with a well-fitting cork. Tie a piece of cotton round a small test-tube by which to lower it into the flask without spilling the contents. Into the flask put some water and pyrogallic acid, into the test-tube put some caustic potash solution; lower the test-tube into the flask without spilling any potash, and keep it suspended by the cotton (Fig. 21). Boil the solution until the steam has expelled all the air, say for one or two minutes, cork the flask, remove the burner, and tip the potash solution into the flask. Allow the air to enter slowly by loosening the cork and note the result. Cork the flask tightly, shake well, and after a few minutes test the gas contained in the flask for oxygen and nitrogen.

We find that nitrogen alone is left, so that a mixture of caustic potash and pyrogallic acid may be used to absorb the oxygen completely from any mixture in which it may be present, provided the solutions are fairly strong.

Exp. 36.—Take a glass tube about 30 cm. long and 2 cm. bore, closed at one end and fitted with an indiarubber cork. Pour in some strong solution of caustic potash (1 in 3) and mark its level by gummed paper. Hold the tube under a tap, or immerse it in a long cylinder of water, while you wrap about a teaspoonful of pyrogallic acid in a small piece of cigarette, tissue, or filter paper. Tilt the tube, place the parcel of pyrogallic acid in the top of the tube, and close it tightly by the cork. Shake the tube at intervals for about 10 minutes. Remove the cork under water, replace it loosely, and transfer the tube to the cylinder of water, keeping the open end down; again remove the cork under water. After a few minutes raise the tube carefully until the water is at the same level inside as out and mark the level with gummed paper. Now run water into the tube from a burette, and note the volumes required to fill the tube to the first mark, to the second mark, and to the open end.

The volume of air actually taken is that contained in the tube between the potash solution and the cork, *i.e.* the difference between the whole volume of the tube and that up to the first paper. The volume of nitrogen left is the volume required to fill the tube to the second paper.

To take an example :—

Volume required to fill tube to first mark = 8 c.c.
,, ,, ,, ,, second mark = 79 c.c.
,, ,, ,, ,, completely = 107 c.c.
∴ ,, of air taken = (107 − 8) = 99 c.c.
∴ ,, of nitrogen left = 79 c.c.
∴ ,, of oxygen = 99 − 79 = 20 c.c.
and percentage of oxygen $= \frac{20 \times 100}{99} = 20{\cdot}2$

As a conclusion we may infer that air consists mainly of a mixture of about 21 per cent. of oxygen with 79 per cent. of nitrogen by volume, together with small quantities of water and a gas which turns lime-water milky, and we have to decide later how these various constituents affect plant and animal life.

31. The Densities of Air and Oxygen.—In Exp. 31 we inferred that oxygen is heavier than air, but we did not make an exact comparison ; we may now pass on to a more accurate determination of the densities of air and oxygen.

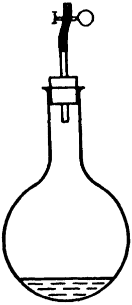
Fig. 22.

Exp. 37.—Take a small (about 250 c.c.) round-bottomed flask and fit it with a tight indiarubber cork, through which passes a short piece of glass tube, over which is slipped a tight piece of india-rubber tube furnished with a pinchcock : the indiarubber tube should be tightly tied on with string or fine copper wire (Fig. 22). Place in the flask about 10 c.c. of water and boil briskly over a small flame after removing the pinchcock. After the water has boiled for two or three minutes adjust the pinchcock to the tube, but keep it open : remove the flame and close the pinchcock at once. Allow the flask to cool, wipe it, and weigh it. Release the pinchcock and weigh again. Remove the cork and fill the flask with water from a measuring cylinder, noting the volume taken.

Since all the air in the flask was displaced by steam, the first weighing is the weight of the flask together with the weight of the water and steam filling it at the boiling point of water. When the flask is cold the steam becomes water, which occupies only about $\frac{1}{1600}$ of the volume of the steam, so that the air which enters practically fills the whole flask except the space occupied by water. The volume actually filled by the air is the volume of water required to fill the flask at the end of the experiment.

Thus since

$$\text{Density} = \frac{\text{Weight}}{\text{Volume}},$$

it follows that :—

$$\text{Density of air} = \frac{\text{Difference of weighings}}{\text{Volume of water required to fill flask}}.$$

To determine the density of oxygen we must introduce a slight variation, thus :—

Exp. 38.—Repeat Exp. 37 up to the first weighing of the boiled-out flask. Fit a bell jar with an indiarubber cork, a short, straight piece of glass tube passing through the cork, a short piece of tight indiarubber tube, a pinchcock, and another short piece of glass tube, preferably with a fine bore. Fill the jar with oxygen in a trough as in Exp. 30. Connect the boiled-out flask with the bell jar by means of the short piece of glass tube and undo both clips (Fig. 23). When the oxygen has filled the flask, close the clips and weigh again. The density is calculated as above.

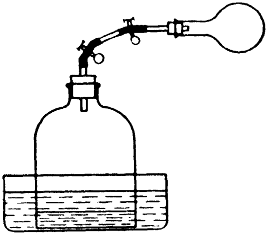

Fig. 23.

The density of nitrogen may be found in a similar way.

32. The Indestructibility of Matter.—In the burning of most of the substances we have examined, one of the characteristics has been the apparent disappearance of some matter, either of the oxygen of the air, of the burning substance, or of both. It becomes important to discover whether the substance which apparently disappears is actually lost or not.

***Exp. 39.**—(*Demonstration Exp.*) Take a 250 c.c. round-bottomed flask and fit it with a tight cork. Put into it a small piece of dry phosphorus, cork, and weigh the flask as it is. Gently warm the phosphorus over a small flame until it lights, and rotate the flask, keeping the phosphorus in motion. When the phosphorus has gone out and the flask is cool, weigh it again, without removing the cork. Now loosen the cork and weigh again. Note the weighings.

We find no change of weight in the closed flask, showing that, though the air seems to disappear, it really does remain in the vessel out of which it appears to go. This is most easily explained by the joining or *combination* of the phosphorus with the part of the air which is used up. If this explanation is correct the phosphorus itself ought to weigh more after burning than before ; this is confirmed by the increase of weight noted in Exp. 39 when air is allowed to enter the flask to take the place of what was used up. Since the flask shows no change of weight on the burning we may infer that the increase of weight of the phosphorus observed when the flask is opened must be exactly the same as the weight of the lost air.

When we repeat any experiment, weighing what we start with and also the products we obtain, we always find that the weights are equal, provided we have been sufficiently careful in tracing *all* the products. This fact is so important that it is termed a law, known as the **Law of the Conservation (Indestructibility) of Matter**, which may be stated thus :— **Matter cannot be created nor destroyed, though it may pass through many different forms.**

CHAPTER IV.

CHARCOAL: CARBON DIOXIDE: CARBONATES: CARBON MONOXIDE.

33. The Burning of Charcoal in Oxygen.—We have already noted that charcoal is one of the substances obtained on heating plants, and we have examined the burning of charcoal in oxygen, and noted the apparent disappearance of the black solid.

Exp. 40.—Take two cylinders and fill them with oxygen. Take two pieces of charcoal (say about 2 c.c.), bind each of them round with a piece of copper wire, passing the other end of the wire through a piece of thick cardboard, light the pieces of charcoal in a Bunsen flame, and lower them into the cylinders. Keep one of the cylinders for the next experiment and into the other pour some clear lime-water.

As we have seen that, though lime-water only turns milky very slowly in air (which contains oxygen), it turns milky at once in the burnt charcoal gas, we may assume that the burning of charcoal in oxygen gives rise to the gas which turns lime-water milky. We can test this by trying to find out if this gas really does contain the black charcoal.

Exp. 41.—Take a piece of magnesium ribbon about 30 cm. long and fold it in three, then twist the three strips together into one. Hold this in a pair of crucible tongs, light one end and lower it into the second jar of oxygen in which charcoal was burned in the last experiment. Burn a piece of magnesium ribbon in ordinary air and compare the ashes. Pour dilute hydrochloric acid on both ashes and compare the results.

We note that the first ash is grey and leaves a black residue in the acid, while the ash which was formed in air is white and leaves no black residue. The black residue when dried and again burnt in oxygen gives a gas which turns lime-water milky, so that the gas formed by burning charcoal in oxygen does really contain the black substance of charcoal. Hence we may infer that when charcoal burns in oxygen it forms a colourless gas which turns lime-water milky, and this gas must be an oxide of charcoal.

Now it does not matter whether we use charcoal, coke, or coal in this experiment, we always note the same effect and the same black residue. We call this fundamental black stuff *carbon*, and the gas which turns lime-water milky *carbon dioxide.*

34. The Action of Acids on Chalk and Marble.—The lime from which lime-water is prepared is made from chalk or limestone, so we will examine these substances more carefully.

Exp. 42.—Place in a test-tube a small piece of chalk or limestone and heat it; when cool pour a few drops of any acid (dilute hydrochloric acid is best) upon it and upon a fresh piece.

We note that no particular effect can be seen from the heating, but that the acid causes a violent fizzing or *effervescence.* To examine this further we proceed as follows:—

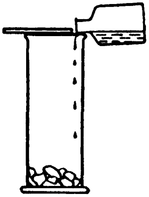

Fig. 24.

Exp. 43.—Take a gas jar and place at the bottom two or three lumps of chalk (whiting) or limestone. Pour upon it some dilute hydrochloric acid and cover the jar with a piece of cardboard (Fig. 24). In a few seconds lower a lighted taper into the jar. Leave the lid off and in a minute test the contents again with the light.

We note that the light is put out at once, even after the jar has been standing with its cover off. This suggests that the fizzing is caused by a gas escaping from the chalk, and also that the gas cannot easily escape from the jar because it is heavy.

Exp. 44.—Repeat the last experiment, keeping the cover on the jar. Try to pour the gas into a cylinder containing nothing but air, being careful not to let any of the liquid run in. Test the new jar with a lighted taper as before. Pour some lime-water into the new jar and shake it.

We find that we have been able to pour into the new jar a gas which puts out a light and turns lime-water milky, so that we can infer that chalk or limestone contains a gas, which is set free by acids, and which is heavier than air, puts out a lighted taper, and turns lime-water milky. This gas must be the same as that formed when charcoal burns in oxygen, and which we have called carbon dioxide.

35. The Preparation and Properties of Carbon Dioxide.—Other solids, such as marble and limestone, are found to have exactly the same reactions as chalk, and may be used in the laboratory as well as chalk for the preparation of carbon dioxide.

Exp. 45.—Take a wide-mouthed bottle of about 300 c.c. capacity. Fit it with a cork bored with two holes, through one of which is passed a thistle funnel and through the other a delivery tube bent twice at right angles (Fig. 25). Into the jar put half a dozen lumps of marble, place an empty gas jar under the end of the delivery tube, which reaches nearly to the table, cover the marble with water, and pour some hydrochloric acid down the funnel. Carbon dioxide is rapidly given off and collects in the jar.

When the gas puts out a lighted taper quite at the top of the jar, cover the jar with a glass plate. Collect five jars of the gas; examine it carefully. (i) Note whether the gas has any colour, taste, or smell. (ii) Into the same jar put a lighted taper. (iii) Pour the gas from one jar into a second jar containing air only, and verify with a taper that the gas is now in the second jar. (iv) Pour some water into another jar, shake it up, and add lime-water. (v) Into another jar pour water, shake up, and then add litmus solution. (vi) Put *two drops* of benzene on a tin or patty pan and light it. Now pour the gas from the fourth jar upon the burning benzene. (vii) Counterpoise or weigh a beaker, pour the gas from the last jar into the beaker, and note the result.

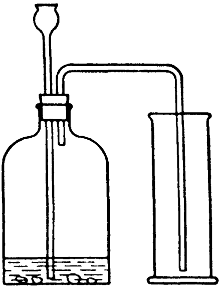
Fig. 25.

From these experiments we note that carbon dioxide is a colourless, heavy gas, with a smell of soda-water, which puts out burning bodies, dissolves in water (see also Exp. 110), and turns lime-water milky, and litmus dull red.

The method of collecting a gas which we have just used, and which depends on its density, is known as *collection by* *displacement.* If we look at the matter from the point of view of the upward movement of the air, we may call it upward displacement, but if from that of the downward movement of the gas, then it may be called downward displacement: it is called *collection by downward displacement* by the majority of chemists.

36. The Action of Acids on Carbonates.—We may now examine the behaviour of some other common substances when acted upon by acids.

Exp. 46.—Place in separate test-tubes some chalk, magnesia, sodium bicarbonate, and washing soda crystals: pour upon them hydrochloric acid, vinegar, and tartaric acid solution respectively. Note any changes, and test any products observed.

In each case carbon dioxide is given off with effervescence. Substances which give off carbon dioxide in this way are called *carbonates*, chalk and marble being called calcium carbonate, magnesia being called magnesium carbonate, and washing soda, sodium carbonate; sodium bicarbonate is already called a carbonate. The further explanation of these names must be postponed for the present, but we can make the general statement:—*When acids are poured upon carbonates, carbon dioxide is given off.*

37. The Action of Acids on Soils.

Exp. 47.—Repeat Exp. 46 using specimens of different soils and dilute hydrochloric acid. Note any fizzing, and test the gaseous contents of the test-tubes by means of a drop of lime water on a clean glass rod (Fig. 26), or by pouring into another test-tube containing clear lime water as in Fig. 27.

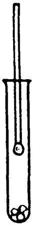

Fig. 26.

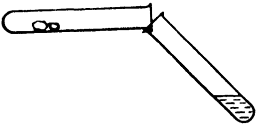

Fig. 27.

In most cases carbon dioxide is given off from the soil, indicating the presence of carbonates.

38. The Action of Carbon Dioxide on Lime-water.—We have used the turning of lime-water milky as a test for carbon dioxide; a white solid is formed.

Exp. 48.—Pass carbon dioxide through about half a litre of clear lime-water. When the milkiness begins to show signs of clearing boil the liquid, filter off and wash the solid, and test it with acid. Put a few drops of the clear filtered liquid on a watch glass and warm it carefully until it evaporates.

Since there is no solid left in the water and a solid carbonate is found in its place, we may infer that the lime, which was made from chalk by heating, has reformed its carbonate, chalk, by the action of carbon dioxide on the lime contained in the lime-water. A solid appearing in this way from a clear liquid is called a *precipitate* and is said to be *precipitated.*

39. The Action of Heat on Carbonates.—We have seen that carbonates readily set free their carbon dioxide when acted upon by acids, though we did not observe any change when we heated chalk in Exp. 42. Repeat the experiment, taking more care over it.

Exp. 49.—Place in a hard glass test-tube some small lumps of chalk and heat the tube over a blast burner, keeping the thumb loosely on the open end. When the chalk is red-hot dip a glass rod or glass tube in clear lime-water and lower it into the tube without touching the sides. Also heat some magnesia, sodium bicarbonate, and washing soda crystals in test-tubes, and test in the same way or by pouring the gas given off into another test-tube containing clear lime-water and then shaking (Fig. 27). In the case of chalk shake up the residue with water, filter, and blow through the liquid (or pass carbon dioxide through it).

It appears that some carbonates are decomposed by heat, giving off carbon dioxide, while others are not, and the relationship between lime and chalk is quite clear, viz. that chalk contains both lime and carbon dioxide joined together, and that the carbon dioxide is given off when chalk is heated, lime being left.

40. The Composition of Carbonates by Weight.—It is now important to find out whether we always obtain the same amount of carbon dioxide from the same amount of chalk, and whether we obtain the same proportion by the action of heat as by the action of acids. We can determine the relationship in two ways, (i) by weight, (ii) by volume, but for our purpose the composition by weight is sufficient.

Exp. 50.—Weigh an empty crucible, put into it about a gram of finely-powdered chalk, or, better, white marble, and weigh again. Place the crucible on a pipeclay triangle and heat it strongly, first over the flame of the blast burner and then by the blowpipe. After it has been heated about twenty minutes let it cool and weigh it. Repeat the heating, cooling, and weighing until the weight has stopped changing.

Calculate the carbon dioxide which would be lost by 100 gm. of the chalk or marble, *i.e.* the percentage of carbon dioxide obtainable from chalk by heating. It is found to be about 44 per cent.

Now find the weight obtainable by the action of acids.

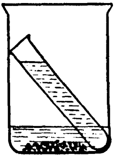

Fig. 28.

Exp. 51.—Take a tall-shaped beaker holding about 250 c.c. and a small test-tube about 2 cm. shorter than the height of the beaker. Weigh the beaker empty, drop into it about 2 gm. of pure dry precipitated chalk and weigh again. Now cover the chalk with water, nearly fill the test-tube with concentrated hydrochloric acid, place it carefully in the beaker, so that it rests against the side without spilling any acid (Fig. 28), and weigh again.

Carefully tilt the beaker so that the acid slowly runs into the water, and when all fizzing has stopped blow out the carbon dioxide by a glass tube, and weigh again.

Enter your results thus :—

Weight of beaker + chalk = 27·25 gm.
,, empty beaker = 25·13 gm.
,, chalk taken = 2·12 gm.

Weight of beaker, chalk, test-tube, water, and acid (before action) = 36·68 gm.

Weight of beaker, chalk, test-tube, water, and acid (after action) = 35·74 gm.

Loss of weight = carbon dioxide = ·94 gm.

∴ percentage of carbon dioxide in chalk

$$= \frac{\cdot 94}{2\cdot 12} \times 100 = 44\cdot 3.$$

A more accurate method of determining this percentage is as follows :—

Exp. 52.—Take a short-necked wide-mouthed flask (about 200 c.c.) and fit it with a cork bored with three holes. Through one hole pass a glass tube reaching to the bottom of the flask and leaving about 2 cm. outside the cork; this tube should be closed by a cap made of a short piece of rubber tube and a short piece of glass rod. Through another hole pass either (*a*) a straight bulb tube filled with calcium chloride, or (*b*) a tube bent in a curve, as in Fig. 29, and fitting the cork of a small calcium chloride tube fixed horizontally. Through the third push a glass rod reaching nearly to the bottom of the flask. Into the flask pour about 1 cm. deep of dilute hydrochloric acid. Weigh a small test-tube and in it place about 1 gm. of pure chalk and weigh again. Take the cork, hold it nearly horizontally, and slip the test-tube over the glass rod. Carefully tilt the flask, and insert the cork and test-tube on its rod. When the cork is tightly fixed weigh the whole, withdraw the glass rod through the cork by twisting it and allow the acid to enter the test-tube slowly. When all the fizzing has stopped warm the flask gently, remove the cap, and suck out the gas in the flask by means of an indiarubber tube slipped over the end of the calcium chloride tube. Replace the cap, and when cool weigh again.

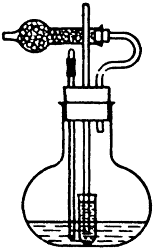
Fig. 29.

The carbon dioxide which is given off is damp, but on passing through the calcium chloride gives up its water to that substance and leaves the apparatus in a dry state; any loss must therefore be due to carbon dioxide only.

The percentage of carbon dioxide in the chalk is calculated in the usual way.

$$\text{Carbon dioxide per cent.} = \frac{100 \times \text{Wt. of carbon dioxide lost}}{\text{Wt. of chalk taken}}.$$

We find that the percentage of carbon dioxide in chalk or marble is the same in both cases, *i.e.* about 44 per cent.

41. The Density of Carbon Dioxide.—The density of carbon dioxide may be determined as in Exp. 38 by finding the weight of carbon dioxide sucked into the empty flask. Another method may also be used, since the gas is much heavier than air.

Exp. 53.—Take a flask fitted with a tight cork and weigh it. Fill the flask carefully with carbon dioxide by displacement (Fig. 30). Remove the delivery tube slowly, put in the cork, and weigh again. Now fill the flask with water and pour the water into a measuring glass in order to find the volume of the flask and the gas.

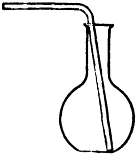

Fig. 30.

At the first weighing of the flask it was full of air, therefore we require to find the weight of air needed to fill the flask under the conditions of the experiment. This is found approximately by multiplying the volume of the flask in c.c. by the value of the density of air (1 c.c. weighs ·0013 gm.). Now if we add this weight to the difference between the weights of the flask full of carbon dioxide and the flask full of air, we obtain the weight of the carbon dioxide filling the flask. Find the density by division, thus :—

$$\frac{\text{Wt. of carbon dioxide in flask}}{\text{Volume}} = \begin{array}{c}\text{Density of carbon dioxide}\\ \text{in gm. per c.c.}\end{array}$$

If we combine the results of the last two experiments, since the weight of the carbon dioxide contained in a given carbonate is constant and the density of the gas is constant, the volume of carbon dioxide given off by the same weight of the same carbonate must also be constant. This fact is often useful in analytical work.

42. Elements and Compounds.—We can now compare the results we have obtained in the examination of reactions in which changes of weight have been noted, and we observe that (i) the sum of the weights of the products is equal to the weight of the original substances, and (ii) each product of decomposition weighs less than the original substance, while (iii) in the case of a combination the product weighs more than each of the original substances.

On examining a large number of substances, we find that some of them, *e.g.* oxygen, nitrogen, and carbon, change their properties by combination only, while others, *e.g.* mercuric oxide, potassium chlorate, chalk, and sodium bicarbonate, change theirs by splitting up into other substances, *i.e.* by decomposition. The former class are called *elements*, the latter *compounds*.

We distinguish between the different members of each group by their own characteristic properties, so that we may define an element as follows :—

An element is a substance finally reached in the decomposition of any material, which has characteristic properties, and which, up to the present, has not been split up into any other substances unlike itself. In this sense the term *split up* includes the idea of weighing less.

A compound also has characteristic properties and can be split up into elements, but it has a further characteristic property based on its composition by weight.

43. The Law of Constant Proportions.—In examining the composition of substances by weight, as in Exps. 50 and 52, we find that each substance always has the same composition however it may be prepared. This result is so important and is confirmed in so many cases that it is stated as a Law, known as **The First Law of Chemical Combination** or **The Law of Constant** or **of Definite Proportions.**

The Law of Constant Proportions is stated as follows :—

The composition of every compound is fixed and definite, or **The same compound always consists of the same elements combined in the same proportions.**

Taking this Law into consideration, we can now give a formal definition of a compound as follows :—

A compound is a substance with characteristic properties, which can be split up into constituent elements, each weighing less than the original substance, but obeying the Law of Constant Proportions.

44. Symbols and Formulae.—It has been found convenient to express the results of chemical observations in a more condensed form than is obtained by the use of ordinary language. In such cases we express the elements by means of letters, sometimes representing their English name, sometimes their classical name ; thus oxygen is written O, nitrogen

N, carbon C, mercury Hg, and magnesium Mg. These letters are called the *symbols* for the elements, and by their means we can write down the composition of a compound. Thus a compound of carbon and oxygen might be written CO, and one of nitrogen and oxygen NO. Such a collection of symbols is called a *formula*. We shall see later that there are many reasons why we should not always be able to use such simple formulae; even the formula for carbon dioxide is written CO_2 (*i.e.* $C + 2O$), though mercury oxide is written HgO and magnesium oxide MgO. Thus when we have been able to decide on a formula for a compound we find it extremely useful for summing up its composition.

45. The Relation of Air to Plant and Animal Life.—We have already noted (in Exp. 1) that when vegetable matter is heated charcoal is left.

Exp. 54.—Fit up two pieces of apparatus as in Fig. 31. In one of them put boiled water and in the other water through which carbon dioxide has been bubbled. Put under each funnel a piece of water-cress and expose both to the light in a window. Test any gases found in the test-tubes by a glowing splint and test the water by lime-water. Repeat the experiment, placing the beakers in the dark.

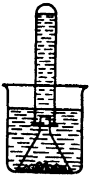

Fig 31.

We observe that, in the light, the green plant removes carbon dioxide from the solution and forms oxygen in its place; it is also found that all green plants act in a similar way.

Exp. 55.—Take a gas jar, a glass plate, and a piece of glass tube a few cm. longer than the jar. Breathe through the tube into the jar. When the jar is full of breath, put on the cover and observe what has happened. Test the contents of the jar by lime-water.

We observe that our breath deposits a film of what appears to be water on the sides of the jar and that our breath is laden with carbon dioxide.

The quantity of carbon dioxide contained in the air is very small and is determined by passing a known volume of air over calcium chloride to dry it, and then over weighed quicklime or through a strong solution of caustic potash (see p. 197). The weight of carbon dioxide is found to be between ·03 and ·04 per cent. of the weight of the air.

Now animals are continually breathing the gas into the air, and it does not seem to accumulate except in closed buildings, so that some agent must be at work removing it as fast as it is formed. The removal is effected by the green plants which replace the gas by an equal volume of oxygen but retain and build up the carbon into their tissues.

Though the percentage of carbon dioxide in the air is so small it amounts to the large total of about 14 tons over each acre of the earth's surface.

Animals remove oxygen from the air in the formation of carbon dioxide.

Exp. 56.—Repeat Exp. 36, using breath instead of fresh air.

It will be found that the oxygen contained in breath may be as low as 16 per cent.

46. The Formation of Carbon Monoxide.—We have all noticed, in the case of a coke or cinder fire burning with a bright red glow, that low reddish or bluish flames play over the top of the fire. As charcoal is made of the same substance (carbon) as coke, and it burns more easily, we may examine the burning of charcoal.

* **Exp.** 57.—(*Demonstration Exp.*) Take a piece of hard glass tube about 25 cm. long, fitted with a cork and a short straight tube at one end, and a cork and delivery tube at the other end; fill it with small pieces of charcoal, and make it red-hot. Attach a test-tube containing potassium chlorate and manganese dioxide to the short tube and pass oxygen slowly through the tube; collect the gas over lime-water (or potash solution) in a test-tube (Fig. 32).

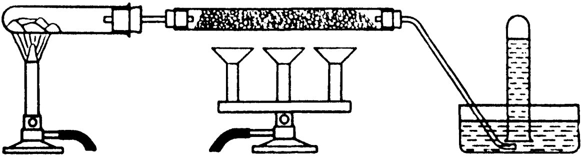

Fig. 32.

When a few c.c. have been collected, apply a light. Test the gas before and after burning by a drop of lime-water on a glass rod, and note what takes place.

It appears, then, that by the action of red-hot carbon on carbon dioxide, which we know is formed by the burning of carbon in oxygen, we are able to prepare a substance which burns with a light blue flame, again forming carbon dioxide. The substance can hardly be anything else than an oxide of carbon, since we prepare it from pure oxygen and pure carbon only.

Other chemical changes may give rise to a gas with properties similar to those of the new gas.

Exp. 58.—Place about 20 gm. of oxalic acid in a flask of about 250 c.c. capacity, fitted with a cork, thistle funnel, and delivery tube for collection of a gas over water. Pour into the flask enough concentrated sulphuric acid to cover the crystals, and warm carefully. Note the reaction, and after all the air is expelled collect the gas given off, over water. Remember to remove the delivery tube from the water immediately you have collected all the gas you want, and put the flask in a draught chamber, or in the open air. Test the gas (i) by a burning taper, (ii) by standing over potash solution. Test a cylinder of gas which has stood over potash by a lighted taper, and afterwards by lime-water. Test also for weight as in Exp. 45.

We appear to have prepared the same gas again, and we recognise it by the fact that it burns in air with a light blue flame to form carbon dioxide. In order to make sure of the nature of the gas, we must burn it with pure oxygen.

Exp. 59.—Take a cylinder of the gas which has stood over potash, and pass some of the gas upwards in the trough into a stout glass explosion tube or a soda-water bottle. Now add about an equal volume of oxygen, wrap the tube or the bottle in a duster, and apply a light. Note what happens, and test the gas left by lime-water.

There appears to be no doubt that the gas which we have prepared contains carbon and oxygen only, and explodes with excess of oxygen to form carbon dioxide; consequently it must contain less oxygen than the dioxide. It is called *carbon monoxide.*

47. Properties of Carbon Monoxide.—In the preparation of carbon monoxide, we note that it is a colourless gas which is not very soluble in water. It possesses a slight metallic smell and is of about the same density as air. It is also a poisonous gas which dissolves in the blood and is difficult to get rid of. Modern coal gas and the producer gas used for gas engines both contain a quantity of this oxide, and must not be breathed.

48. **Oxidation.**—In the burning of carbon with oxygen to form carbon monoxide and the burning of carbon monoxide with oxygen to form carbon dioxide, the resulting carbon compounds contain relatively more oxygen than the originals ; such a process is called an *oxidation.*

CHAPTER V.

EFFECTS OF HEAT: TEMPERATURE: LAWS OF BOYLE AND CHARLES.

49. Introductory.—Up to the present we have noted that certain changes are brought about by the action of heat, *e.g.* the decomposition of vegetable matter, the decomposition of mercury oxide. We have also noted that some bodies become hot when they are undergoing changes, *e.g.* quicklime when slaked by water, charcoal when burning in oxygen. In order to find out more about these heat effects we must first examine cases in which no permanent or chemical change seems to be brought about.

50. Temperature.—The first effect we notice when we apply a flame to a body or put it near a fire or in the sunlight is that it gets warm or hot, by which we generally mean that it gives the sensation which we call heat to the skin when touched. Similarly, if we touch a lump of ice or dip a finger into iced water, our skin becomes chilled, and we receive the sensation which we call cold.

On warming the iced water it gradually changes from feeling cold to feeling hot. The relative hotness or coldness of bodies is called their relative *temperature*, and temperature is more exactly defined as the state of a body in respect of its power of receiving heat from or imparting heat to other bodies. Our sensations cannot be used for more than rough comparisons of temperature, and then generally only for temperatures at which our skin and nerves can remain alive, so we must examine some effects of heating bodies which do not depend on our sensations.

51. Effect of Heating Solids.—One important change produced by heating solids is seen in a change of size.

Exp. 60.—Take a sphere of metal which will just pass through a metallic ring (Fig. 33), and make the sphere hot in a Bunsen flame. The sphere will not now pass through the ring until it has cooled or the ring become hot.

The metal has expanded on heating. On cooling it contracts to its original size, and it exerts force in doing so. Use is made of this in the tightening up of cart wheels by shrinking on the iron tyre. The tyre is made too small to fit the wheel, and then made hot until it just fits over the wooden rim. On cooling, the tyre contracts and pulls the whole wheel together.

The actual expansion of small solids when heated is too small to be seen, but it can be magnified by the use of a lever, and can then be measured; the solid grows larger as it becomes hotter.

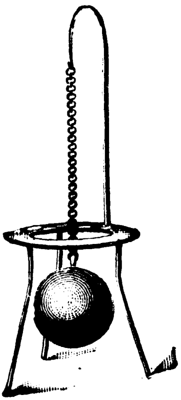

Fig. 33.

52. Expansion of Liquids.—When liquids are heated in open vessels, it is not easy to see whether they expand or not, but if a tall vessel or jug is filled to the brim with boiling water and then allowed to cool, it is seen that the jug is not full when the water has cooled. We may examine this carefully.

Exp. 61.—Nearly fill a long test-tube with water, and mark the level of the water by fixing a strip of gummed paper on the test-tube so that the upper edge of the paper appears just to touch the lowest point of the meniscus. Hold the tube over the flame of a Bunsen burner until the water is hot, and then examine the level of the water. Allow the water to cool and examine it again.

We observe that, after heating, the lowest point of the meniscus is slightly above the upper edge of the paper, showing that the water has expanded; it returns to its original volume on cooling. The expansion is visibly larger than that of a solid of the same length, and it can readily be magnified by transferring the expanded portion to a tube of smaller bore.

Exp. 62.—Take a large test-tube or a small flask, and fit it with a cork through which passes the end of a piece of glass tubing of narrow bore. Completely fill the test-tube or flask with water, and insert the cork so as to make the liquid rise a short distance in the narrow tube (Fig. 34). Then place the test-tube or flask in a beaker of hot water. Remove the test-tube from the hot water and allow it to cool.

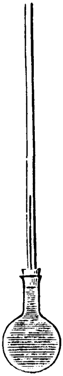
Fig. 34.

We observe that on heating the test-tube the water rises some distance in the narrow tube. Since the diameter of this tube is much less than that of the test tube, a given volume of liquid occupies a much greater length of the narrow tube than of the test tube, and therefore the small increase in the volume of the water due to the heating causes a considerable rise of the water in the narrow tube. Again the liquid returns to its original volume on cooling.

53. Effect of Rise of Temperature on Density.—In Chapter II. we have seen that the density of any substance $= \frac{\text{weight}}{\text{volume}}$, so that when the volume of a solid or a liquid is increased by heating, it follows that its density is reduced. In the case of milk this reduction of density is of importance, while in the case of water the change in density produced by the heating effects of the sun sets in motion currents in the oceans, which carry heat from the equator towards the poles.

54. Expansion of Gases.

Exp. 63.—Fit up a small dry flask with a cork and narrow glass tube as for Exp. 62. Place the open end of the tube in a beaker of water, and warm the flask by holding it in the hands. Note what happens (Fig. 35). Then allow the flask to cool and again note what happens.

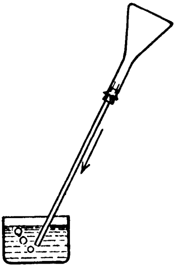
Fig. 35.

We observe that, when the flask is warmed, air bubbles out through the water from the open end of the tube, showing that the gas, air, expands when heated, as do solids and liquids. When the flask cools again, water rises in the narrow tube, showing that the air has contracted. It should be noted that the very gentle warming by means of the hand produces a large expansion, indicating that gases expand more on heating than do solids or liquids.

Expansion of gases by heating causes changes of density just as in the case of liquids, and this may be seen in the fire balloon. Such a balloon is filled with air, and has an opening in the bottom of the envelope, below which cotton wool soaked in spirit is lighted. The heat of the flame warms the air in the balloon, so that it expands and some of it escapes. The warm air in the balloon is lighter than the air surrounding it, and the balloon therefore rises. A similar effect is produced when a fire is lighted at the bottom of a chimney, the lighter hot air inside being forced upwards by the cooler air outside.

Movements of the atmosphere (*i.e.* winds) are also caused by unequal heating. The air over regions of the earth which are strongly heated becomes warmed, decreases in density, and rises, thus causing currents of air to flow in from the surrounding regions.

55. Comparison of Temperatures.—In the preceding experiments it has been noted that solids, liquids, and gases all expand on heating, and return to their original size on cooling again, so that the amount of the change in size may be used as a measure of the temperature to which the hot body has been raised. That is, we can use a given increase in length of a solid or a given increase in volume of a liquid or a gas as a measure of a temperature change, provided we always use the same solid or liquid or gas ; then when a temperature is reached at which the body is observed to show half its original increase in size, we can say its temperature has risen half the original rise, and so on.

Changes in length of a solid are generally too small to be useful without very delicate magnifying apparatus ; changes in the volume of gases are rather too large for convenient use; but changes in the volume of a liquid contained in a bulb fitted with a narrow neck or stem as in Exp. 62 are easy to make visible and to compare, and this arrangement is generally used in the construction of *thermometers* for the comparison of temperatures.

56. Thermometers.—In constructing a thermometer from a liquid enclosed in a glass bulb and tube, some points of practical interest arise.

Mercury or alcohol is generally used as the liquid. Mercury freezes at a low temperature and boils at a high temperature, does not wet the tube, and soon reaches the temperature of its surroundings. Alcohol, on the other hand, though it boils at a much lower temperature than mercury, also freezes at a much lower temperature; it wets the tube.

The bulb of the thermometer is either spherical or cylindrical, most generally the latter in a chemical thermometer, so that the diameter may be the same as that of the tube for passing through corks. After the bulb is filled the liquid is generally sealed in the bulb and tube so as to avoid loss by shaking or evaporation.

In order to obtain a scale of temperature differences which will agree in the case of different thermometers, some standard temperatures must be taken as fixed. Different standards have been used, but only two are now generally adopted, the melting point of ice, and the boiling point of water when the barometer stands at a height of 760 mm. (29·9 inches).

The melting point of ice may be marked on the thermometer, or verified if already marked, by covering the bulb of the thermometer with broken ice in a funnel (Fig. 36). It is generally called the *freezing point*.

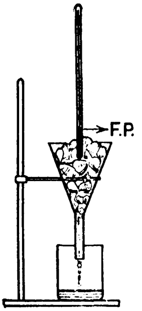

Fig. 36.

The *boiling point* of water is conveniently determined or verified by supporting the thermometer in the neck of a long-necked distilling (Wurtz) flask so that it hangs centrally down the neck (Fig. 37). The bulb should be a little below the exit tube, and as much of the stem as possible should be surrounded by the steam in the neck.

If the barometer stands below 760 mm. the boiling point will read too low, if above 760 mm. too high (see p. 99).

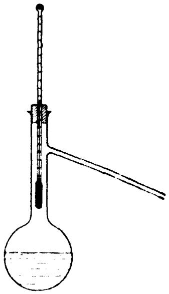

Fig. 37.

There are three methods of making scales of temperature on the basis of these two standard or fixed points of temperature, viz. the Centigrade, Fahrenheit, and Réaumur scales (Fig. 38).

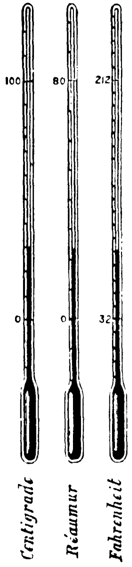

Fig. 38.

The *Centigrade* scale is the one most generally used for scientific purposes. On it the freezing point is taken as zero, and marked 0°; the boiling point is marked 100°. The space between the fixed points is then divided into 100 equal divisions, called *degrees*. Graduation on the same scale is extended beyond the reference points; divisions below zero, *i.e.* below freezing point, are considered negative, and those above zero positive.

The *Fahrenheit* scale was introduced by Fahrenheit, of Danzig, about the year 1714. On it the freezing point is marked 32° and the boiling point 212°, the space between being divided into 180 equal degrees, and the division extended above and below the fixed points. In this method of division, the zero is at a point 32° below the freezing point; it indicates what was supposed in Fahrenheit's time to be the lowest attainable temperature—that obtained by mixing snow and sal-ammoniac. The temperature marked 100° is approximately the temperature of the human body. The Fahrenheit scale is generally used in this country for the purposes of ordinary life, and, to some extent, for those of science.

On the *Réaumur* scale, the freezing point is taken as 0°, and the boiling point is marked 80°. There are thus 80 equal divisions between the fixed points on this scale, which is used in several European countries for ordinary purposes.

57. Conversion of Thermometer Scales.—In changing the expression of a temperature in one of these scales to its equivalent in either of the other scales, we have to remember that between the freezing and boiling points there are in the Fahrenheit scale 180 divisions, in the Centigrade 100, and in the Réaumur 80, or :—

$$\text{F.} : \text{C.} : \text{R.} = 180 : 100 : 80 = 9 : 5 : 4.$$

In order to change from Centigrade to Réaumur, we have simply to multiply by $\frac{4}{5}$ and, to change from Réaumur to Centigrade, by $\frac{5}{4}$. Thus :—

$$15^\circ\ \text{C.} = \frac{15 \times 4}{5} = 12^\circ\ \text{R.}$$

$$-8^\circ\ \text{C.} = \frac{-8 \times 4}{5} = -6{\cdot}4^\circ\ \text{R.}$$

In changing from Centigrade or Réaumur to Fahrenheit, if we multiply by $\frac{9}{5}$ or $\frac{9}{4}$, we shall get the number of Fahrenheit degrees *above the freezing point*, and to this we must add 32 because Fahrenheit's scale begins 32° below the freezing point. For example :—

$$80^\circ\ \text{C.} = \frac{80 \times 9}{5} + 32 = 176^\circ\ \text{F.}$$

$$-30^\circ\ \text{C.} = \frac{-30 \times 9}{5} + 32 = -22^\circ\text{F.}$$

Finally, to change from Fahrenheit to Centigrade or Réaumur, we must first subtract 32, and then multiply by $\frac{5}{9}$ or $\frac{4}{9}$. For example :—

$$240^\circ\ \text{F.} = \frac{(240 - 32)5}{9} = 115{\cdot}6^\circ\ \text{C.}$$

$$= \frac{(240 - 32)4}{9} = 92{\cdot}4^\circ\ \text{R.}$$

$$28^\circ\ \text{F.} = \frac{(28 - 32)5}{9} = -2{\cdot}2^\circ\ \text{C.}$$

$$= \frac{(28 - 32)4}{9} = -1{\cdot}8^\circ\ \text{R.}$$

$$-20^\circ\ \text{F.} = \frac{(-20 - 32)5}{9} = -28{\cdot}9^\circ\ \text{C.}$$

$$= \frac{(-20 - 32)4}{9} = -23{\cdot}1^\circ\ \text{R.}$$

58. Maximum and Minimum Thermometers.—In agricultural and horticultural work we often require to know the highest and the lowest temperatures reached in a building or in the open air, without the trouble of watching the thermometer. For this purpose *maximum and minimum thermometers* are used. They are chiefly of two types :—

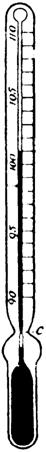

Fig. 39.

(i) The *clinical thermometer*, which is used to obtain the body temperature of man or farm animals when disease is suspected. This is a maximum thermometer, indicating the highest temperature it has reached (Fig. 39). It is a mercury thermometer with a relatively large bulb and narrow tube, and has a range of about 20° F., say 90°-110° F. (the normal temperature of the human body is 98·4° F.; of horses, 100·6° F.; cattle, 101·9° F; sheep, 104° F.; pigs, 103° F.). A constriction is formed in the bore of the tube near the bulb, as shown at *c* in Fig. 39. The mercury in expanding is readily pushed through the constriction, but on contraction the mercury thread is pulled and breaks there, so that the top of the mercury column remains at the highest reading reached by the thermometer. The instrument can be set for another reading by shaking until the mercury again joins up into a single column.

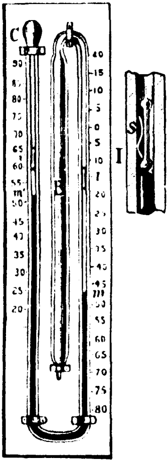

Fig. 40.

(ii) The moveable index type, of which the most generally used is *Six's thermometer*. In this thermometer the stem is very long and is bent into an elongated coil as in Fig. 40. The expanding liquid is spirit, and as it expands it moves a long mercury index, the other end of which is in contact with spirit moving freely into and out of a half-filled bulb. The movements of the mercury are recorded by small steel dumb-bells provided with weak springs which prevent their moving by themselves in the spirit. They are, however, moved by the curved ends of the mercury column, thus recording the nearest and farthest movements of these ends, and so the minimum and maximum temperatures reached. The steel indexes are easily moved by a magnet when required.

In the preceding cases as well as in the case of all spirit and most other common thermometers the scale of temperature is fixed by comparison with a standard thermometer.

59. **Atmospheric Pressure.**—That the atmosphere exerts a pressure can be shown by sucking the air from the top of a tube standing in water or any other liquid, when the pressure of the atmosphere causes the liquid to rise in the tube. The pressure appears to be limited, since by sucking out the air by means of a pump, the water can only be made to rise in the tube about 34 feet or 10 metres, and mercury can only be made to rise about 30 inches or 760 mm. The downward pressure of both these columns is about 14½ lb. per sq. inch or 1000 gm. per sq. cm.

It is very much easier to remove the air from the top of the tube by filling the tube with mercury as in Exp. 64 than by pumping the air out.

Exp. 64.—Take a dry glass tube about 33 in. long and closed at one end, and fill it completely with mercury. Close the open end with the finger, invert the tube with its open end in a cup of mercury, and remove the finger, taking care that no air is allowed to get into the tube. Note what happens, and measure the height of the column of mercury in the tube (Fig. 41).

Fig. 41.

We observe that the mercury sinks, leaving a clear space at the top of the tube, and that the height of the column of mercury above the mercury surface in the cup is about 30 inches or 760 mm. The simple instrument thus made enables us to measure the pressure of the atmosphere at any time and place, and is a simple *barometer*.

60. Effects of Pressure on Gases. Boyle's Law.—It is found that the pressure of the atmosphere as indicated by the barometer is continually changing, that it gets less as we ascend a hill, and gets greater as we descend a mine. Changes in the height of the barometric column also tell us a great deal about atmospheric changes.

Change of pressure affects the volume of a gas, as is seen when a test-tube of air is placed with its open end just touching the surface of some water in a deep cylinder and then pushed downwards : as the tube descends, the water rises inside the tube, showing that the increase of pressure causes a diminution of the volume of the air.

Since a change in the volume of any gas causes a change in its density, and the accurate value of the density of a gas is of great importance in chemistry because, in addition to its fundamental character, it enables us to determine the weight of any measured volume of a gas, *e.g.* the weight of oxygen obtainable from a given weight of potassium chlorate, it is necessary to know the connection between the volume of a gas and the pressure it exerts. The relationship can be investigated experimentally as follows :—

Exp. 65.—Take a glass tube about a metre long and 5 mm. bore, close one end, and bend the closed end quite round about 20 cm. from the end until it makes a U-tube with a short closed and a long open limb (Fig. 42). Pour a little mercury into the tube through a funnel and shake until the mercury stands at the same level in both limbs of the U. Measure the volume of air in the closed limb (= length of air column × area of tube, which is constant and may be taken as = 1), and read the level of the mercury by measuring its height above a fixed horizontal surface, *e.g.* the bench. Pour in some more mercury and measure the volume of air and the difference between the levels of the mercury columns. Repeat several times until the mercury nearly reaches the top of the open limb. Read the height of the barometer.

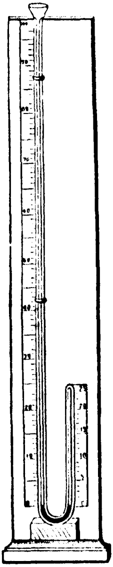

Fig. 42.

Your results (in centimetres) should be entered in a table, thus :—

Level of top of closed limb.	Level of mercury at bottom of closed limb.	Level of mercury in open limb.
14·2	2·2	2·2
	3·4	11·0
	4·7	23·3
	6·4	46·0
	7·3	61·9
	8·05	76·5
	8·7	92·8

By subtracting the second column from the first the relative volumes of the closed portion of air are found, and by subtracting the second from the third the heights of the mercury column which bring about these changes of volume : enter these volumes and mercury columns in the first two columns of another table, thus :—

Volumes ($=v$)	Mercury columns ($= h$)	$h + 75{\cdot}2 = p$	$v \times p$
12·0	0	75·2	902
10·8	7·6	82·8	894
9·5	18·6	93·8	891
7·8	39·6	114·8	895
6·9	54·6	129·8	896
6·15	68·45	143·65	884
5·5	84·1	159·3	876

Now the differences in the mercury levels or the different heights of the columns of mercury really cause differences of pressure in the air contained in the closed limb, and as the air in the closed limb itself starts under the barometric pressure while the air continues pressing with the same pressure on the mercury in the open limb, we can get the total pressure on the air in the closed limb by adding the barometric height (in this case 75·2 cm.) to the height of the mercury column. Enter these total pressures in the third column of the table.

We note that as the numbers in the first column decrease those in the third column increase, and we may try the effect of multiplying together corresponding numbers in the two sets. Enter the results in the fourth column.

We observe that the products are nearly constant, and our results may be stated thus : the product obtained by multiplying the volume of a closed portion of air by its total pressure is constant.

This relationship is stated in the form of **Boyle's Law** :— **The volume of any gas varies inversely as its pressure if the temperature is not changed.** Expressed symbolically, if V is the volume of any gas under the pressure P, and V' its volume under the pressure P',

then $$\frac{V}{V'} = \frac{P'}{P},$$

or $$VP = V'P'.$$

For convenience of comparison it is usual to choose some standard pressure to which to refer all gas volumes, and the standard accepted in chemistry is that of a column of mercury 76 cm. high ; this is a convenient standard, since it is about an average value of the atmospheric pressure.

61. Change of Volume and Temperature Changes.—We have already seen in Art. 54 that a gas expands when heated, so that change of temperature, as well as change of pressure, alters the density of a gas.

The determination of the relationship between volume and temperature is very important. For our purpose the simplest experimental method will suffice.

Exp. 66.—Take a piece of glass tube of about 2 cm. bore and 50 cm. long and fit it with a loose two-holed cork at one end and a tight one-holed cork at the other. Through the single hole pass a short tube provided with a short piece of indiarubber tube and a clip, and through the other cork pass (i) a piece of narrow-bored glass tube about 50 cm. long and drawn to a point, and (ii) a thistle funnel reaching nearly to the other end (Fig. 43).

Now remove the cork and narrow-bored tube, put the open end of the tube under mercury, and suck a bead of mercury about 2 cm. long into the tube: allow the bead to run down the tube to about 25 cm. from the point, and seal the point in the gas flame. Press the tube with the bead carefully through its cork until the closed end is about 5 cm. from the end of the wide tube, and suspend a thermometer so that its bulb is about midway between the closed end and the bead. Place a graduated scale behind the apparatus.

Fill the wide tube with cold water by means of the funnel, read the length of the column of air enclosed by the bead, and the temperature of the water. Take a large flask of water about 20° hotter than the cold water, empty the wide tube by the pinchcock, and pour in the hot water through the funnel; read the new volume of the air and the temperature of the water in the tube. Repeat this series of operations, using hotter water each time until you reach a temperature of about 90° C.

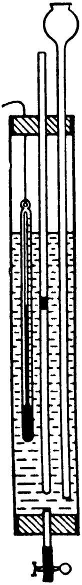
Fig. 43.

Your results should be entered in columns as in the first columns of the table below :—

Temperature $= t$	Volume $= v$	Changes of temperature starting from 15° C.	Changes of volume starting from 23 c.c.	$\frac{\text{Change of temp.}}{\text{Change of volume}}$
15°	23	0	0	—
25	24	10	1	10
44	25·8	29	2·8	10·4
60	27	45	4	11·2
74	28·1	59	5·1	11·6
91	29·7	76	6·7	11·3

We note that as the temperature rises the volume also rises, but it is evident that the volume itself does not increase as quickly as the temperature. We can, however, try the effect of dividing the changes of temperature by the changes of volume produced. Thus, taking our standard volume of 23 c.c. at 15°, we can set out a series of new temperature and volume differences, which should be arranged in the third and fourth columns of the table.

The two sets of numbers are now seen to be nearly related and very nearly proportionate to one another ; the relationship is more clearly brought out by dividing the temperature changes by the volume changes produced and entering the results in the fifth column. Though these numbers are not quite the same, they are sufficiently so to suggest that the observed expansion of volume of a gas is proportionate to the rise of temperature causing it.

This inference is converted into a certainty by repetition and by means of other experiments. It is found to be true for all gases, and is conveniently stated as **Charles's Law** :—**The volumes of all gases expand by the same proportion for equal increments of temperature, if the pressure is not changed.**

In order to make the changes strictly comparable it is usual to fix a standard temperature for which we can calculate a fixed fraction, *the coefficient of expansion of a gas.* This standard temperature is taken as 0° C. The proportion by which all gases starting at 0° C. do expand for a rise of temperature of 1° C. is 0·003665, or more conveniently $\frac{1}{273}$.

The latter number gives us another way of looking at the volume changes, since, if a gas were to continue to keep its own properties, it would gradually diminish when cooled, and finally disappear at — 273° C. Thus the volume of a gas may be considered to be exactly proportionate to its temperature reckoned from — 273° C., and *Charles's Law* may be stated in another way :—**The volume of any gas varies directly as its temperature reckoned from — 273° C., if the pressure is constant.**

Since all gases expand at the same rate, while liquids and solids expand at different rates, there are many advantages in using a temperature scale which is independent of the substance used. Such a scale is called a scale of *absolute temperature,* and — 273° C. is taken as the zero of absolute temperature.

It is convenient to write Charles's law symbolically. Thus, if V is the volume of any gas at $t°$ and V' is its volume at $t'°$, then when the pressure is constant

$$\frac{V}{V'} = \frac{t + 273}{t' + 273},$$

or

$$\frac{V}{t + 273} = \frac{V'}{t' + 273}.$$

[*Note.*—The above results for the temperature-volume and pressure-volume relationships may be more neatly reached by *plotting* the experimental results on squared paper.

In this method the object is to produce a straight line from the experimental numbers, either directly, or indirectly by adding a constant to, multiplying, or squaring, etc., one of the quantities, and plotting the new values again, until a straight line relation is obtained.

In the above cases, for (i) *the temperature-volume relationship*, the temperatures may be plotted horizontally and the volumes vertically. The volumes are at once found to lie in a straight line, which when produced below zero cuts the no-volume line about − 250° (more accurately about − 270°). This is seen to agree with the relationship that the volume is proportionate to the temperature + 273°. For (ii) *the pressure-volume relationship*, the pressures may be plotted horizontally and the volumes vertically, when the volumes are found to lie on a curve. Now divide each pressure value into 1, obtaining fractions representing $\frac{1}{p}$, and plot again these values with the corresponding volumes. The volumes are now found in a straight line, so that v is proportionate to $\frac{1}{p}$, or v is inversely proportionate to p.]

Charles's Law may be combined with that of Boyle, so that we can calculate the volume of a gas when both temperature and pressure vary. The relationship obtained is

$$\frac{VP}{t + 273} = \frac{V'P'}{t' + 273}.$$

This formula is very important and must be remembered.

We have selected as our standard temperature and pressure 0° C. and a vertical column of 760 mm. of mercury, so that our combined equation for correcting any volume of a gas to standard conditions of temperature and pressure becomes

$$\frac{V \times 760}{273} = \frac{V'P'}{t' + 273},$$

where V is the volume under standard conditions of 0° C. and 760 mm. pressure, and V' is the volume of the same gas measured at any temperature t'° and pressure P' mm. of mercury.

As an example, suppose we have found in Exp. 37 that the weight of air in the flask = 0·30 gm., and that its volume is 243 c.c. at 15° C. and 755 mm. pressure, and we wish to find the correct density of the air.

First, substitute in the equation, thus :—

$$\frac{V \times 760}{273} = \frac{243 \times 755}{15 + 273} = \frac{243 \times 755}{288},$$

from which $$V = \frac{243 \times 755}{288} \times \frac{273}{760}$$

$$= 229 \text{ c.c.}$$

Now density $$= \frac{\text{Weight}}{\text{Volume}}$$

$$= \frac{0{\cdot}30}{229}$$

$$= 0{\cdot}0013 \text{ gm. per c.c.}$$

CHAPTER VI.

WATER: HYDROGEN.

62. The Examination of Natural Waters.—The greater part of the surface of the earth is covered by the sea; at frequent intervals rain falls on the land, part of which disappears or sinks and rises again from the ground in the form of springs, and part runs off, joining with spring water to form brooks and at last streams and rivers.

In everyday life we include these liquids under the common name of water, for though they differ in some ways, yet they all appear to be similar in many other respects. If they are muddy, after being allowed to settle they become clear, colourless liquids, which freeze and boil like water.

Let us examine these kinds of water and try to find out whether they contain a definite chemical substance.

Exp. 67.—Take three clean watch glasses and put into them five drops of sea water, rain water, and spring water respectively. Evaporate them over a tiny flame and note any differences in quantity, appearance, and taste of the residues.

We note that the different waters leave on evaporation different residues, so that we must look for uniformity elsewhere. Let us try to regain the liquids which have apparently disappeared.

Exp. 68.—Take a small flask and put into it some sea or other natural water. Fit the flask with a cork, bored with one hole, through which passes a long piece (50 cm.) of tube, bent at an angle as in Fig. 44. Put another flask over the end of the tube, stand it in a basin of cold water, and boil the water in the first flask. Repeat the experiment, using another kind of water, and collect what comes over in another flask. Now evaporate five drops of each specimen from the collecting flasks on clean watch glasses and taste the specimens themselves.

In each case no residue is left on evaporation, and the specimen tastes like rain water, so that the specimens are possibly the same substance. The process just described is called *distillation*, and the water which collects is called *distilled water.*

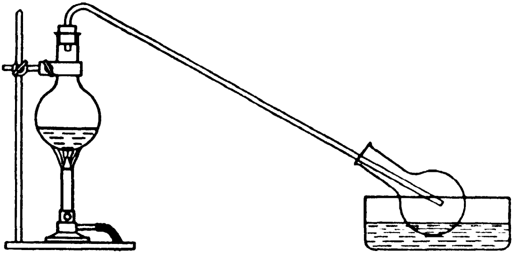

Fig. 44.

It will have been noticed that the long tube becomes very hot, and that a great deal of steam escapes. We can prevent this loss of steam by cooling the long tube by means of a cold water jacket.

Exp. 69.—Take a wide tube of about 3 cm. bore and fit it with two corks bored with two holes. Pass through the corks a longer tube so that its ends project at each end of the wide tube, and through the other holes pass two short tubes bent at right angles. Now take a flask containing water as in the previous experiment, but fitted with a short tube through the cork instead of a long one.

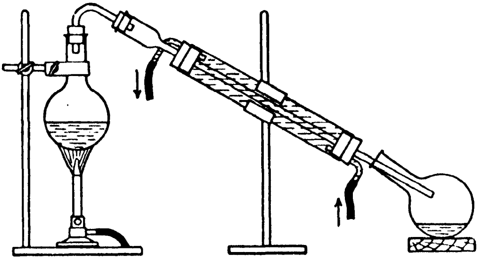

Fig. 45.

Connect the flask with the inner straight tube by means of a piece of indiarubber tubing or a cork, and fix the apparatus as in Fig. 45. Connect the lower short tube with a water tap and the upper with a sink, and keep a small stream of water running through. Heat the flask.

We note that hardly any steam now passes right through the inner tube, and that the water running into the sink is warm. Such an apparatus is called a *Liebig's condenser*, or, more shortly, a *condenser.*

63. The Composition of Water.—In starting the examination of the properties of water, we may remember the fact that metals rust and tarnish in damp air, and so we may examine the action of metals on water.

Exp. 70.—Place pieces of iron, zinc, copper, lead in water and examine them from time to time.

Some of these metals show slow changes which may possibly be helped by heating.

***Exp.** 71.—(*Demonstration Exp.*) Take a piece of thin-walled combustion tubing about 10 cm. long, fitted with one cork bored with one hole. Through this cork pass one end of a piece of glass tubing bent at right angles, of which the other end is passed through the cork of a small flask containing water (Fig. 46). In the tube place some magnesium powder. Heat the flask carefully until the water begins to boil, then heat the tube and powder to prevent the condensation of water from the steam. When hot, light the magnesium at the open end of the tube and boil the water. Note any changes in the magnesium and in the steam.

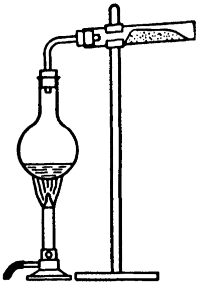
Fig. 46.

We observe that the magnesium goes on burning in the steam much as it does in air, until it is all converted into a white powder, but that the steam also appears to burn. These facts suggest the possibility that, as in the case of carbon dioxide (Exp. 41), the burning of the magnesium may have removed oxygen from the steam and produced something else which will burn. In order to pursue the investigation further, we must make the reaction more manageable.

Exp. 72.—Place about a teaspoonful of magnesium powder in a mortar and add to it a drop of mercury. Rub them well together. Now place the mixture in a beaker filled with water, and insert a funnel with a short stem, upside down, in such a way as to cover the metal. Fill a test-tube with water and invert it over the end of the funnel, as in Fig. 47. Warm the beaker and watch the test-tube. When the bubbles of gas have filled the tube, close the end with your thumb, remove the tube from the water, and apply a light to the mouth of the tube as soon as you remove your thumb. Prepare another tube of the gas; remove it, using your thumb as before, and, keeping the mouth down, place a dry test-tube mouth to mouth with the other. Remove the thumb and turn the first test-tube gradually downwards until it is mouth upwards under the dry tube. Separate the tubes and apply a light to each.

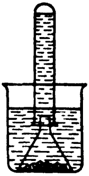

Fig. 47.

[*Note.*—The action may also be examined by putting the magnesium into an upright flask fitted with a delivery tube, as in Exp. 68, and filling the flask quite full of water before inserting the cork. The gas is then collected over water.]

We note that there is a gas given off which burns when lit, that it rises from the lower test-tube into the upper, so that it is evidently lighter than air, and that its burning is accompanied by the appearance of mist on the dry tube.

Hence we appear to have been able to prepare from water as well as from steam a gas which burns in air, is lighter than air, and appears to form water when it burns in air.

In order to find out whether the last inference is correct we must prepare the new gas on a larger scale and test the product formed on burning it for water.

64. Tests for Water.—We have already found in our first experiments (Exp. 2) that anhydrous copper sulphate turns blue on contact with water.

Exp. 73.—Moisten a filter paper with a solution of the chloride or sulphate of cobalt and dry it carefully over a small flame, noting any changes. Now put drops of water and other liquids, such as alcohol, paraffin oil, turpentine, on the filter paper and note the effects.

Copper sulphate crystals turn colourless when heated, and we observe that cobalt solutions turn blue when dried, and that water is given off. Water restores the blue colour to the copper sulphate and the pink colour to the cobalt paper, while the other liquids do not bring about these changes. Hence we may assume that we can use these two substances as *tests for water*, the test being that if the liquid turns dried colourless copper sulphate blue and dried blue cobalt chloride and sulphate pink, it is water.

65. The Action of Dilute Acids on Metals.—We can now proceed with our search for the gas which burns in air.

> **Exp. 74.**—Take some pieces of magnesium ribbon in a test-tube and pour in some dilute hydrochloric acid : apply a light to the tube. Collect the gas given off by putting the metal in a test-tube, filling the test-tube with water and inverting it, quite full, closed by the thumb, in a dish of dilute hydrochloric acid. Test the gas as in Exp. 72 by pouring the gas into a dry test-tube, lighting it, and testing the product with colourless copper sulphate. Repeat the experiment, using zinc and iron respectively in place of magnesium, and also dilute sulphuric acid in place of hydrochloric acid.

In each case we note that the metal disappears or dissolves in the liquid, and that the same gas appears, which is lighter than air and burns to form water. This gas is the same as that prepared by the action of magnesium in contact with mercury on water, and is called *hydrogen*. We have also found a method of preparing the gas on a scale large enough for examination.

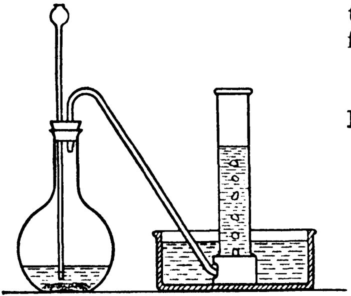

Fig. 48.

66. The Preparation and Properties of Hydrogen.

> **Exp. 75.**—Take a wide-mouthed bottle or a flask of about 300 c.c. capacity and fit it with a good well-softened cork. Bore two holes through the cork : through one hole pass a thistle funnel just far enough to reach within $\frac{1}{2}$ cm. of the bottom, and through the other a tube bent for the collection of a gas over water in a pneumatic trough (Fig. 48). In the bottle place about 25 gm. of granulated zinc, replace the cork tightly,*

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* If any difficulty is found the cork can be easily inserted if the bottle is held horizontally.

cover the zinc with water till about 2 cm. deep, and then pour in hydrochloric acid or dilute sulphuric acid through the thistle funnel.

Collect the gas at first in a test-tube and test it by means of a burning taper, after removing it some way from the trough. When the gas burns quietly in the tube instead of popping, collect four jars full. (i) Examine the first jar carefully, for colour, taste, smell, etc. (ii) Remove the second jar from the trough, keeping it mouth downwards, and apply a lighted taper to the mouth ; then thrust the taper right up into the jar and again withdraw it. (iii) Remove one jar from the trough, covering it first with a glass plate ; stand it mouth upwards and remove the cover. Test it in 10 seconds with a lighted taper. (iv) Stand a beaker mouth downwards on one pan of a balance and counterpoise it ; remove the beaker, pour the last jar of hydrogen up into it, and replace it on the pan, noting any difference of weight.

The results of these experiments confirm those noted in Exp. 72 in the case of the gas obtained from water, so that we can identify hydrogen as a colourless, scentless gas which is much lighter than air and burns readily with a colourless or bluish flame.

67. Combustion.—Before passing on, we may compare the behaviour of hydrogen, carbon monoxide, and carbon when they combine with oxygen. In all the cases we have noted (i) that the burning is accompanied by the production of a high temperature, resulting in flame, explosion, or quiet burning, and (ii) that the changes accompanying the liberation of heat are chemical changes. A chemical change which produces a temperature high enough to enable us to see that the burning body is hot is termed a *combustion*, and the term is often confined to changes of this kind, brought about by combination with oxygen only.

68. The Density of Hydrogen.—Since we have determined the density of oxygen, nitrogen, and carbon dioxide, we ought to determine the density of hydrogen before passing on.

Exp. 76.—Repeat Exp. 53, using as large a flask as you can weigh, but fill the dry flask held bottom up with hydrogen (upward displacement). Weigh the flask full of air and full of hydrogen, find its volume, and calculate the density as described.

It will be noted that the difference between the weighings is very small, so that the results obtained by a class may vary a great deal. In fact 1 c.c. of hydrogen measured at 0° C. and 760 mm. pressure weighs only 0·00009 gm.

Another source of error will now suggest itself, viz. that the gas may be wet; the bottle in which it is made generally becomes warm, and the gas becomes steamy; the gas is certainly damp then, and may be so even when it is cooler. The gas can be dried as in the next experiment.

69. **The Synthesis of Water.**—We have already seen on a small scale that water is formed when hydrogen burns in air, so that we should confirm the observation on a larger scale; but since, as we have just seen, water is present in the hydrogen apparatus, we must make sure that it is all removed from the gas before the hydrogen is allowed to burn. We can use quicklime for this purpose as before (Exp. 16).

Exp. 77.—Fit up or use the apparatus for preparing hydrogen as in the last experiment. Fit a straight or U-tube of about 1 in. bore with two corks through which are passed short tubes, and nearly fill the tube with lumps of quicklime.* Attach one of the short tubes to the hydrogen apparatus and the other to a short piece (3 or 4 cm.) of clay-pipe stem, by means of india-rubber tubes.

Now fit a flask with a cork and two tubes, one long and one short, the longer of which is connected with the water tap and the shorter with the sink, so that a stream of cold water can be kept passing through the flask; fix the flask in a clamp (Fig. 49). Start the hydrogen, and when it has been

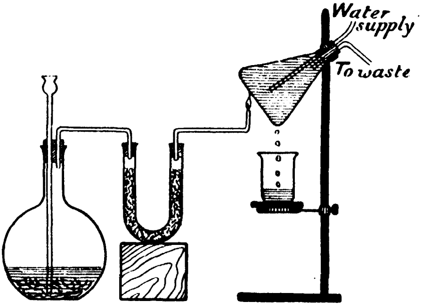

Fig. 49.

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* Calcium chloride freshly dried is also convenient to use for drying hydrogen in this way, and a small bottle fitted with a cork through which are passed two tubes bent at right angles, one long enough to reach nearly to the bottom of the bottle and the other only just passing through the cork, is a convenient substitute for a drying tube. The bottle is nearly filled with lumps of quicklime or calcium chloride.

coming off for some time, place a test-tube over the pipe stem and test for the presence of air, as in Exp. 75.

When all the air is removed, light the gas at the pipe stem jet, and adjust the flask over the flame so that it plays on the bottom of the flask rather to one side. Collect any liquid formed by allowing it to drop into a watch glass or beaker, and test it with copper sulphate and cobalt chloride as before.

Water is thus formed when dry hydrogen burns in air.

We have up to the present considered the hydrogen as burning simply in the air, but we ought to make certain whether the oxygen and the nitrogen are both required for the synthesis of water.

Exp. 78.—Prepare a jar of oxygen as in Exp. 30, but keep it dry by collecting the gas by displacement as in Exp. 45. Now bend a delivery tube as in Fig. 50, and attach it to the pipeclay jet used in the last experiment. Attach the delivery tube to the drying tube, and when the apparatus is found to be free from air, light the gas at the jet and lower it alight into the jar of oxygen. Note what takes place and test any drops seen on the sides of the jar by copper sulphate and cobalt chloride as before.

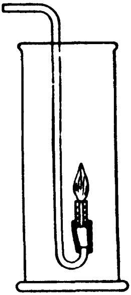

Fig. 50.

We note that hydrogen burns with the oxygen alone to form water, so that water is made up of hydrogen and oxygen only.

[This inference may be confirmed by mixing dry hydrogen with dry oxygen in a dry explosion tube and lighting the mixture carefully. Drops of liquid appear on the sides of the tube and may be tested as above. Further confirmation as to the part played by the air may also be obtained by repeating the last experiment, using a jar of nitrogen in place of oxygen.]

70. Chemical and Physical Changes.—In comparing the formation of water by the burning of hydrogen and oxygen with the formation of carbon dioxide by the burning of carbon in oxygen, we note three important features.

(i) Hydrogen is a light gas which burns in air but does not allow things to burn in it, and oxygen is a gas slightly heavier than air which does not burn but does allow things to burn in it ; in the combination, steam is first formed, then a drop of water, which is a liquid which does not burn but puts burning things out. The properties of water thus present a marked contrast to those of the hydrogen and oxygen which make it up.

Similarly, carbon is a black solid which burns in air, oxygen is a gas slightly heavier than air which does not burn nor affect lime-water but allows things to burn in it, while carbon dioxide is a gas much heavier than air which does not burn, extinguishes burning bodies, and does turn lime-water milky.

These differences are summed up by saying that when a chemical combination takes place the properties of the product or products are different from those of the constituents ; or chemical action is accompanied by a *change in the properties* of the combining substances.

(ii) The steam and the carbon dioxide do not again change their properties until they undergo chemical change, *i.e.* the *change of properties* noticed on chemical combination *is permanent.*

(iii) When hydrogen and oxygen combine we notice a flash or hot flame, and when carbon combines with oxygen we also note that *heat is given out.*

Hence we can state that a *chemical change* is a change which is attended by a permanent change in the properties of the substances undergoing the change and also by a heat change.

We have already examined one very characteristic chemical change when we heated grass in Exp. 1, and many other examples of chemical change will be studied later.

Other changes of properties may also be observed which are not chemical changes, but they can generally be distinguished from chemical changes by the absence of one of the three characteristics previously mentioned.

Exp. 79.—(i) Put a weighed piece of platinum foil in a flame. Note what you see, let the foil cool, and weigh it again.

(ii) Place a small quantity of mercuric iodide in a test-tube, weigh it, and warm it gently in a flame. Note what you see, let the tube cool, and weigh it again.

(iii) Connect a battery with an electric bell by means of a weighed piece of copper wire. Weigh the wire again, and also test it by connecting the bell terminals with it.

In the first experiment the foil changes colour and gives out heat when in the flame, but it regains its original colour and weight when removed. In the second we note a temporary change of colour without change of weight. In the third we note a temporary change of properties without change of weight. So that, though we notice one or more of the characteristics of chemical change in each of the changes, yet we always find one or more characteristics missing. In order to distinguish such changes from chemical changes they are called *physical changes.*

71. The Composition of Water by Volume.—We have already found that chalk always contains the same percentage of carbon dioxide, so that it is important to find out whether the percentages of hydrogen and oxygen which combine to form water are also constant. Since both the constituents of water are gases, it would be easiest to start by an examination of their relation by volume.

Exp. 80.—Take a funnel cut with a short, wide neck and fit it with an indiarubber cork through which pass two pieces of platinum wire, each threaded lengthwise through a strip of platinum foil about 3 cm. by $\frac{1}{2}$ cm. Fill the funnel with water made acid by a little sulphuric acid, cover each strip by a test-tube full of the dilute acid, and connect the two platinum wires with the poles of a battery consisting of two or three cells (Fig. 51). Note what takes place. When one test-tube is full of gas mark the level of the water in the other by gummed paper. Remove the test-tubes after closing them with the thumb, and then test each gas by a lighted taper and glowing splint. Measure the volumes of the gases in the test-tubes by a burette as in Exp. 36.

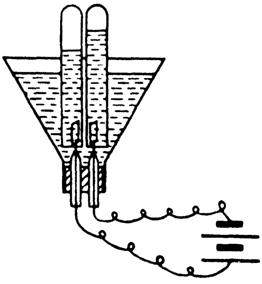

Fig. 51.

We observe bubbles forming on the platinum wires ; these bubbles gradually become bigger and rise into the test-tubes, but one gas collects more quickly than the other. On testing, the gas of larger volume is found to burn, while that of less volume makes the glowing splint burst into flame, so that these gases are probably hydrogen and oxygen. The volume of the hydrogen is found to be about twice as great as that of the oxygen, but we must not assume without confirmation that this is the relation in which they combine, since sulphuric acid is present as well as water.

Exp. 81.—Repeat Exp. 80, using hydrochloric acid instead of sulphuric acid, and afterwards using sodium sulphate.

Since the only constituent present in all three cases is water, and the products are always the same, we are justified in making the inference that the hydrogen and the oxygen are derived from the water, and that the volume relation just observed between the hydrogen and oxygen must be that between the same gases in water, viz. 2 : 1. The apparatus thus described is termed a *voltameter*, and many other kinds of voltameter are used.

We can also use another method, in which only hydrogen and oxygen are present, for the determination of the composition of water by volume, viz. to explode a mixture of hydrogen and oxygen only, in a closed tube, and measure the volumes of each gas used in the formation of water.

Exp. 82.—Take a U-shaped graduated tube called a *eudiometer*, with one end closed and with two platinum wires sealed into the closed end. Fill the tube with water. Take a piece of india-rubber tube a few centimetres longer than one limb of the U-tube and attach to one end the delivery tube of an apparatus giving off pure hydrogen. Put the tube into the open limb of the eudiometer, and when all air is expelled from the hydrogen apparatus lower the tube into the open limb until about 10 c.c. of the gas passes round the bend into the closed limb (Fig. 52). Remove the gas tube, level the water in the two limbs with the help of a pipette, and measure the hydrogen; let us assume that it measures 10 c.c.

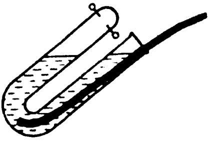
Fig. 52.

Now repeat the process, using oxygen instead of hydrogen, and run the gas in until about twice the hydrogen volume has been run in. Level and read the volume as before (say it measures 28 c.c.). Fill the open tube with water to within about

2 cm. of the top, and either cork it tightly or hold it with the thumb firmly pressed on the open end. By means of an induction coil or electric gas lighter pass a spark between the platinum wires, keeping the thumb pressed on the open end or the cork. After the explosion, remove the thumb or cork carefully, level the columns, and measure the residue again (say it measures 13 c.c.). Fill the open limb with water again, close it with the thumb, decant the residual gas into the open tube, and test it with a glowing splint.

We note that the residue consists of oxygen, so that the total loss of volume (or contraction) is equal to the volume of the hydrogen (which has all been used up) together with the volume of that part of the oxygen which has been used.

Thus

$$\begin{aligned} \text{hydrogen used} &= 10 \text{ c.c.}, \\ \text{oxygen used} &= \text{contraction} - \text{volume of hydrogen} \\ &= (28 - 13) \text{ c.c.} - 10 \text{ c.c.} \\ &= 5 \text{ c.c.} \end{aligned}$$

That is, 10 c.c. of hydrogen have combined with 5 c.c. of oxygen to form water, or the ratio of hydrogen to oxygen by volume = 2 : 1.

72. The Composition of Steam by Volume.—We have just seen that water is formed by the combination of hydrogen and oxygen in the ratio of 2 : 1 by volume. In order to complete our knowledge of the composition of water by volume, we ought to find the ratio of the volume of the water formed to that of the gases used. One point of difficulty immediately arises, viz. that water can only be compared with gaseous hydrogen and oxygen in its gaseous form, steam, that is above 100°.

Unfortunately the manipulation of gases above 100° is not easy, and steam is particularly difficult to deal with unless well above that temperature, so that it will be sufficient for our purpose to state the results which were obtained when the density of steam was determined above 100° and compared with the density of a mixture of hydrogen with half its volume of oxygen at the same temperature.

In one experiment 49·7 c.c. of steam (corrected for temperature and pressure) were found to weigh ·041 gm., or the density of steam (calculated at 0° and 760 mm.) $= \frac{\cdot041}{49\cdot7}$ $= \cdot00082$ gm. per c.c.

The density of a mixture of hydrogen with half its volume of oxygen was also determined and 282 c.c. (corrected) were found to weigh ·1555 gm. This makes the density of the mixed gases (calculated at 0° and 760 mm.) $= \frac{\cdot1555}{282} =$ ·00055 gm. per c.c.

Now by the law of the conservation of matter we require ·00082 gm. of the mixed gases to make 1 c.c. of steam, and this weight occupies $\frac{\cdot00082}{\cdot00055} = 1\cdot5$ c.c.

In other words, 3 c.c. of the mixed gases or 2 c.c. of hydrogen and 1 c.c. of oxygen must combine together to form 2 c.c. of steam at the same temperature.

This is a most important result, and it will be considered carefully in Chapter IX.

73. Solution, Filtration, Crystallisation.—In addition to the important properties of water which we have considered there are many others which are of very great use to us.

Exp. 83.—Take some sugar, salt, chalk, and sand, and place them in test-tubes with distilled water. Shake up well for a minute or two. Note the differences in behaviour of these substances. When the liquids are clear taste them. Also take some coloured solids such as potassium dichromate and cadmium yellow (cadmium sulphide) and shake them with water; allow them to stand and note any differences. Also take some liquids such as alcohol, ether, paraffin, and olive oil, and shake them with water; note any differences.

In some cases the substances appear to impart their properties to the water and are said to *dissolve* in the water. When two liquids mix, either may be said to dissolve in the other.

We note that the solids which do not dissolve appear to settle to the bottom and remain in the form of small particles. We can test this by straining off the particles by passing the liquid through a strainer with very small holes, such as those which are found in muslin, calico, or, smaller still, in blotting (filter) paper.

Exp. 84.—Take a circle of filter paper about 15 cm. in diameter and fold it in half along a diameter ; now fold it in half again at right angles to the diameter in such a way as to make a quarter of a circle. On looking at the curved edges it will be seen that two conical pockets can be formed ; open out one of them and place the paper in a glass funnel, thus forming a conical *filter* (Fig. 53) : moisten the paper with water to make it adhere to the funnel. Repeat the last experiment (Exp. 83) with the solids only and pour all the waters on filters. Examine all the liquids which pass through as before, and also by placing a few drops of each liquid on separate watch glasses and evaporating them slowly over a tiny flame. Observe whether they leave a solid residue or not.

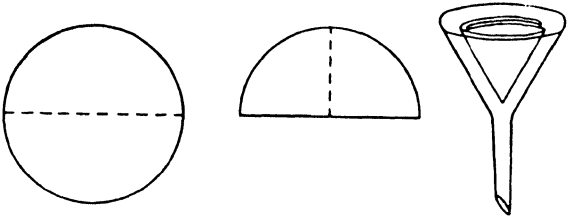

Fig. 53.

An intimate mixture of a solid and a liquid, which passes unchanged through a filter paper and possesses the properties of both constituents, is called a *solution*, and the substance which dissolves is said to be *soluble* in the liquid *solvent*. The process of passing the solution through a filter paper to remove solids is termed *filtration*.

A mixture of a soluble and an insoluble solid can be separated by means of a solvent.

Exp. 85.—Take a mixture of powdered alum and sand. Boil the mixture with water in a basin and filter it. Place the solution (*filtrate*) in an evaporating basin on a saucepan of boiling water with a sheet of tinplate on the top, out of which a hole has been cut to support the basin with its bottom in contact with the steam. This arrangement is called a *water bath* (Fig. 54). Keep the water in the saucepan boiling by means of a gas flame. The water in the basin slowly evaporates; when a scum appears on its surface put it aside to cool slowly. In the meantime wash the sand on the filter with water until the water which passes through no longer tastes of alum; take out of the funnel the filter paper and sand and put them on a pad of blotting-paper to dry. Examine the solution when cold.

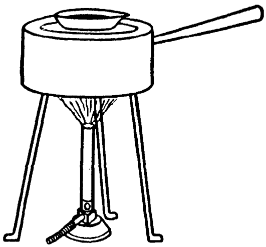

Fig. 54.

We note that small, shining solids with a regular shape and flat faces have been deposited from the solution; these solids are called *crystals*, and they increase in size when they are allowed to stand in the solution. A solution which is depositing crystals is said to be *saturated*, and the liquid from which the crystals have been formed is called the *mother liquor*. The process of forming crystals is termed *crystallisation*, and the more slowly crystals are formed, the larger do they grow.

We have thus separated our mixture and obtained crystals of pure alum free from sand, and also pure sand free from alum.

Exp. 86.—Take some powdered saltpetre and blue vitriol and dissolve them separately in water. Allow them to crystallise slowly and form large crystals. Examine and compare the crystals.

74. Natural Waters.—We are now in a position to examine the differences between some natural waters.

Exp. 87.—Evaporate 20 c.c. of each of the natural waters, rain water, spring water, and sea water. Examine the residues and note the differences.

Exp. 88.—Fit a large test-tube with a cork and a tube bent at right angles, fill it with any natural water, and boil. Pass the gases and steam given off through lime-water. Note the presence or absence of carbon dioxide.

Exp. 89.—Fit a large flask of about 1 litre capacity with a cork and tube bent for collecting a gas over water. Fill both flask and tube completely with water which has been well shaken with air, and fix the flask on a tripod stand with the end of its delivery tube under a test-tube which has been filled with lime-water and then inverted in a small basin of water. Now heat the water in the flask and note the appearance of any gas. As soon as steam comes over quickly, stop the heating and test the gas contained in the test-tube by a glowing splint. Repeat the experiment, using natural waters.

We note that bubbles gradually appear as the water gets warm, and that when collected in the test-tube they make the splint glow brightly. Hence we believe that the gas boiled out of the water contains oxygen as well as carbon dioxide, so that natural waters contain dissolved gases, in addition to various dissolved solids. The different solids and the varying properties of the gases give to the waters their peculiar differences.

75. Water in its Relation to Plant and Animal Life.—Water is of fundamental importance to plant and animal life. In the first place it appears to enter into the composition of all living matter, of which it makes up nearly three-fourths of the total weight; this water can be removed from living matter by exposure to dry air or warmth, causing the death of the living tissue without any other recognisable chemical change. Partial drying, as in the wilting of plants, may be recovered from by the taking up of water again. This water appears to act as a whole and not specially as a compound of hydrogen and oxygen.

In the second place water appears to supply hydrogen for the building up of living matter; this hydrogen appears partly in the form of water, when dried tissues are decomposed by heat (Exp. 1).

In the third place, water is necessary to living matter as a solvent of food materials, which only undergo the necessary changes when in solution. This aspect will be considered more fully later.

76. Expansion of Water by Heat.—We have already seen that the melting point of ice appears to be a fixed temperature, and is taken as a standard point on thermometric scales (0° C. or 32° F.), and also that the boiling point is fixed when the atmospheric pressure is constant, and is taken as a second standard temperature (100° C. or 212° F.). In spite of this, water is not used for filling thermometers, and this important point must be examined further.

Exp. 90.—Fit a four-ounce flask as in Fig. 34 (Exp. 62) and fill it and about 3 in. of the tube with ice-cold water from melting ice. Immerse it in a large beaker of ice-cold water standing on wire gauze on a tripod stand and measure the height of the water in the tube above the cork. Then warm the water in the beaker by means of a Bunsen burner, and read the temperature of the water and the height of the water in the tube at equal intervals of time, say 2 min. Plot your results on squared paper to show the relation of volume and temperature.

We note that as the water in the flask gets warmer it contracts for a short time, but on further heating, and while the water is still very little warmer than at first, the contraction ceases, and is replaced by expansion, which quickly restores the original volume. The expansion continues as the water is heated, and appears to become relatively greater towards the boiling point. This experiment indicates that there is a point, not far from the freezing point, at which a given quantity of water occupies a minimum volume, and that the rate of expansion increases with the temperature, especially near the boiling point.

The temperature at which the volume is a minimum is called the *point of maximum density* of water. In the metric system this point is of great importance, since water at its maximum density is the standard substance from which the unit of weight (mass) is defined and to which all other densities of solids and liquids are referred.

The determination of the actual point of maximum density is a matter of some difficulty, but it is found to be very nearly 4° C.

A simple form of *Hope's experiment* illustrates some important practical results.

Exp. 91.—Take a tall tin or glass jar surrounded at its centre with an outer vessel and fitted with two thermometers as shown in Fig. 55. Fill the jar with cold water and the outer vessel with a freezing mixture. Read the temperatures on both thermometers at intervals of one minute, and plot the results.

We note that as the water cools under the influence of the freezing mixture, the temperature of the lower thermometer falls steadily, while that of the upper one undergoes but little change. The temperature of the lower thermometer falls more and more slowly as it approaches 4° C., and then becomes stationary. After this the temperature of the upper thermometer falls more rapidly, and continues to fall until 0° C. is reached. Ultimately a crust of ice begins to form on the surface of the water, while the temperature of the lower thermometer remains stationary at 4° C.

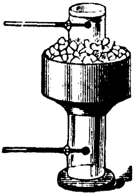

Fig. 55.

This experiment illustrates what actually takes place in pools of water or waterlogged land during frosty weather; the surface freezes, but the temperature of the deepest layer of water seldom falls below 4° C., a temperature at which animal life is not always destroyed. In the spring the heat of the sun may raise the surface temperature sufficiently to allow growth before the subsoil is heated above 4° C.

CHAPTER VII.

QUANTITY OF HEAT: SPECIFIC HEAT.

77. Quantity of Heat.—Many common observations suggest that there is another characteristic of heat besides temperature. In pouring boiling water into cold water to produce a warm bath, the more boiling water is added, the warmer is the mixture : the boiling water cools and the cold water becomes warmer. Also if we pour equal quantities of boiling water into different quantities of cold water, different temperatures are produced, the smaller quantity of cold water reaching the higher temperature. Similarly, water is sometimes boiled by dropping hot stones into it.

It appears that there is a characteristic property of hot bodies in virtue of which they are able to heat colder substances to different temperatures, in spite of their having the same temperature themselves. This property is generally considered to be a quantity, and depends upon the weight of the hot body as well as its temperature.

Since the quantity of heat depends on these two factors, we can consider it as depending on the product

weight × temperature.

78. Effects of Heat upon Different Substances.—When we examine land on which the sun has been shining, we often notice that the stones are warmer than the soil, and that a dry soil is warmer than a wet one. We notice, too, that other things being equal, a gravel soil is earlier than a loam and a loam than a wet clay soil. To examine a possible cause :—

Exp. 92.—Take three beakers or metal cans and place in them equal weights, say 100 grams, of water, sandy soil, and iron filings respectively. Put a thermometer in each, and stand the beakers on a sand bath or asbestos sheet heated by a Bunsen burner. Read the temperature on each thermometer every minute, stirring vigorously before reading.

Enter your results in a table thus:—

Time of heating in minutes.	Temp. of water.	Temp. of soil.	Temp. of iron filings.
0	18°	18°	18°
1	25°	34·5°	41°
2	33°	51°	59°
3	39°	66°	76°
4	45°	77°	90°
5	51°	87°	99°
6	56°	96°	108°

We note that the rate of rise of temperature is different in the three cases, the temperature rising most slowly in the case of the water, and most rapidly in that of the iron filings, although equal weights of all three substances were taken, and heat has been supplied to each by the same sand bath and probably at the same rate. We thus see that the same amount of heating does not produce an equal rise of temperature in all substances.

The results of the experiment may be plotted in a graph such as that shown in Fig. 56, in which temperatures are plotted against times of heating.

The graph for each substance is roughly a straight line at the lower temperatures, equal times of heating causing approximately equal rises of temperature. Now take any convenient temperature interval, say from 30° C. to 50° C., and determine from the graph the time taken to produce this rise of temperature in each of the three substances. For water the time is 3·2 minutes, for the soil 1·25 minutes, and for iron filings 1·0 minute. We can infer that the quantities of heat required to raise equal weights of water, soil, and iron filings through the same interval of temperature are roughly in the proportion 3·2 : 1·25 : 1·0, or 1 : ·39 : ·31.

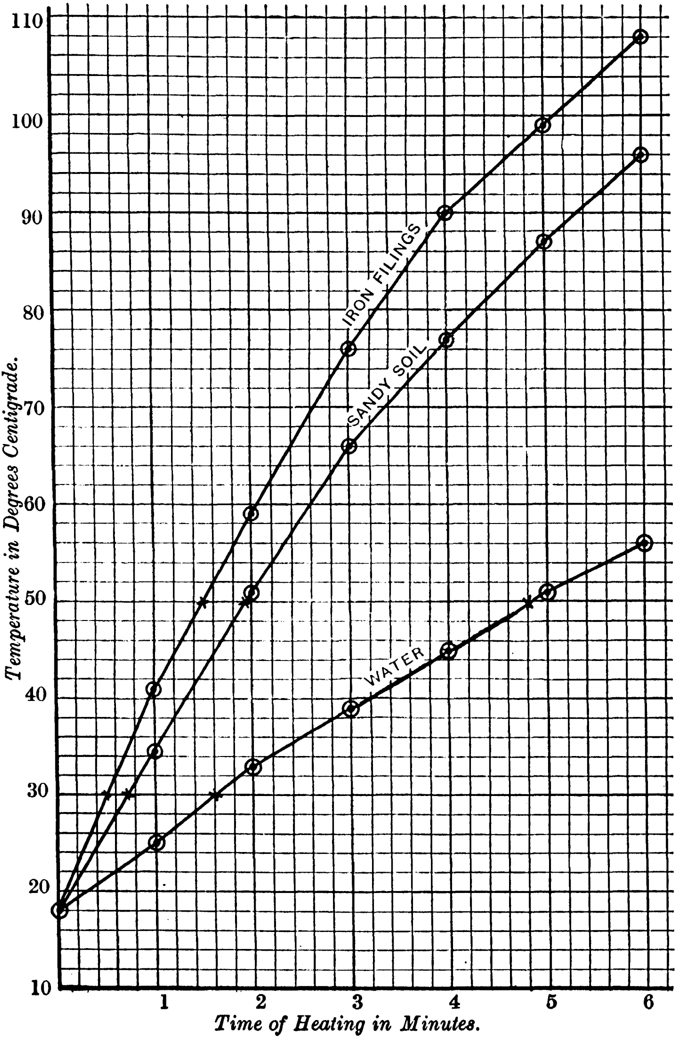
110
100
90
80
70
60
50
40
30
20
10
Temperature in Degrees Centigrade.
IRON FILINGS
SANDY SOIL
WATER
1
2
3
4
5
6
Time of Heating in Minutes.

Fig. 56.

79. The Unit of Heat.—We can determine ratios of other quantities of heat and express them in respect of any selected substance as a standard. Water has been adopted as the standard (= 1), but it is more convenient to select a definite unit. For this purpose the quantity of heat required to raise the temperature of 1 gm. of water through 1° C. is chosen as the unit in scientific work; this unit is called a *calorie*. Thus in the last experiment, in rising from 30° to 50°, 100 gm. of water required $100 \times 20 = 2000$ calories, 100 gm. of dry sand $2000 \times {\cdot}39 = 780$ calories, and 100 gm. of iron filings $2000 \times {\cdot}31 = 620$ calories.

In feeding experiments on animals this unit is too small, and the larger unit of the quantity of heat required to raise the temperature of 1000 gm. of water from 0° to 1° C. is used; it is called the *large calorie* or *Calorie*, and is equal to 1000 small calories.

In engineering work where the pound and the Fahrenheit scale of temperature are used, the unit is the *British Thermal Unit* or B.Th.U., which is the quantity of heat required to raise the temperature of 1 lb. of water through 1° F.

It should be noted that the heat required to raise the temperature of 1 gram of water through 1° C. is not exactly the same at all temperatures, so that for strict accuracy the temperature rise should be specified, and has been fixed from 0° to 1° C. The temperature effect is, however, very small, and can be neglected for our work.

80. Specific Heat.—In the last experiment we found that the quantities of heat required to raise equal weights of water, dry soil, and iron through the same temperature range were in the ratio 100 : 39 : 31; the ratios when carefully determined are found to be constant for the same substances, and should be 100 : 24 : 11 in the case of water, sandy soil, and iron.

If we take the quantity of heat required to raise the temperature of 1 gm. of water through 1° C. as 1 calorie, then the heat required to raise the temperature of 1 gm. of the dry soil through 1° C. is ·24 cal., and the heat required to raise the temperature of 1 gm. of iron through 1° C. is ·11 cal. These numbers are called *specific heats*.

As the numbers are also ratios, we can also define the specific heat of a substance as

$$\frac{\text{Heat reqd. to raise any wt. of the subs. thr. any temp. range}}{\text{Heat reqd. to raise same wt. of water thr. same temp. range}}.$$

This gives the same numerical value as the preceding definition, and the ratio applies to any unit of weight or temperature.

Since the quantity of heat required to heat any body depends on its specific heat as well as on its weight and the temperature rise, we can now state that the quantity of heat required to raise the temperature of a body through any temperature range, or which it can give out in falling through any temperature range

= weight of the body × change of temp. × specific heat.

81. Determination of Specific Heats.—Perhaps the simplest method of accurately determining specific heats is the method of mixtures.

Exp. 93.—Weigh a thin copper or aluminium beaker, called a *calorimeter*, pour in cold water until it is about two-thirds full, weigh it again, and stand it on a dry piece of cork or cotton wool. Place a thermometer in the calorimeter and read the temperature. Take a piece of iron, *e.g.* an iron nut from a $\frac{3}{4}$ in. bolt, and pass a piece of cotton through the hole. Lower it into a beaker of water, kept boiling by a flame. After a few minutes read the temperature of the boiling water, pull the nut quickly out of the beaker by the cotton, shake off any adhering drops of water, and lower the nut at once into the calorimeter. Stir the water in the calorimeter by means of the thermometer and read the highest temperature reached.

Enter your results as follows :—

Weight of (aluminium) calorimeter = 20·5 gram.
" " " and water = 134·7 "
∴ Weight of water = 114·2 "
Weight of iron nut = 87·5 "
Temperature of iron = 99·5° C.
" " cold water = 14·3° C.
" " mixture = 20·8° C.

In this experiment the hot iron has lost heat, and the cold water has gained heat.

$$\begin{aligned}\text{Heat lost by iron} &= \text{wt. of iron} \times \text{specific ht.} \times \text{fall in temp.}\\ &= 87{\cdot}5 \times S \times (99{\cdot}5 - 20{\cdot}8)\\ &= 6886\ S \text{ calories.}\end{aligned}$$

The heat gained by the cold water = wt. × rise in temp.

$$= 114{\cdot}2 \times (20{\cdot}8 - 14{\cdot}3) = 742 \text{ calories.}$$

If the whole of the heat lost by the iron nut has been used in heating the water, we can say

$$\text{heat lost by iron} = \text{heat gained by water}$$

$$6886\ S = 742$$

or

$$S = {\cdot}108 \text{ calories.}$$

But there is one important loss of heat which must be considered, viz. the heat taken up in raising the temperature of the calorimeter and the thermometer as well as of the water. It is easy to deal with the calorimeter loss, since that = weight of calorimeter × specific heat × rise of temperature, so that a better equation would be

$$\text{heat lost by iron} = \text{heat gained by water and calorimeter}$$

$$\begin{aligned}\therefore\ 6886\ S &= 742 + 20{\cdot}5 \times {\cdot}22 \times 6{\cdot}5\\ 6886\ S &= 742 + 29\\ 6886\ S &= 771\\ S &= {\cdot}112 \text{ calories.}\end{aligned}$$

The heat taken up or given out by the calorimeter for a change of temperature of 1° C. is called the *water equivalent* or *heat equivalent* of the calorimeter.

There are other sources of error: (*a*) heat is lost by the hot body during its transfer from the boiler to the calorimeter; this is minimised by quickness of working, (*b*) heat is gained by the water and calorimeter if the hot body is not dry; this can be prevented by heating in an oven instead of in boiling water, (*c*) heat is lost by the calorimeter heating the surrounding air; this is overcome in many ways, the simplest of which is to wrap the calorimeter in dried cotton wool after weighing it with the cold water in. The best method is to use a vacuum (thermos) flask. The calorimeter should always be kept polished.

82. Specific Heat of Soils.—In agricultural work we are chiefly interested in the specific heat of soils, as the earliness of a soil largely depends on that ratio. As a fertile soil contains a considerable but variable percentage of water, we must first dry the soil. We can then use the method of mixtures if we place the soil in a boiling tube with a thermometer buried in it, and then heat it in a saucepan of boiling water. The soil may be poured from the tube into the calorimeter, and the results worked out as in the last experiment.

Another method can be used, as follows:—

Exp. 94.—Half fill a boiling tube with dry soil and place a thermometer in it: read the temperature of the soil. Weigh a calorimeter, and fill it about half full of water at a temperature of about 40° C. Weigh the calorimeter and water and read the temperature exactly. Pour the dry soil into the calorimeter, stir, and read the temperature.

Enter your results thus:—

Weight of (aluminium) calorimeter = 36·3 gram.
" " and water = 136·3 "
" " and dry soil = 196·3 "
∴ Weight of water = 100·00 "
Weight of dry soil = 60·0 "
Initial temperature of water and calorimeter = 45° C.
Initial temperature of dry soil = 15° C.
Final temperature of water and dry soil and calorimeter = 41·5° C.

Then since

heat gained by soil = heat lost by water and calorimeter

$$60 \times S \times (41{\cdot}5 - 15) = (100 + 36{\cdot}3 \times {\cdot}22)(45 - 41{\cdot}5)$$

$$60 \times 26{\cdot}5 \times S = 108 \times 3{\cdot}5$$

$$\therefore S = \frac{108 \times 3.5}{60 \times 26{\cdot}5} = {\cdot}24.$$

This method is typical of a measurement involving a loss of temperature and is subject to the error that some of the loss may be due to the cooling of the warm water in the calorimeter. A correction can be easily applied by repeating the experiment and noting the loss of temperature per minute, and making the necessary correction for heat loss during the time the experiment is going on until the final temperature is read.

83. Effect of Water in Soils.—The specific heat of a moist soil is partly due to the water content, partly due to the soil, and is often more interesting than the specific heat of the dry soil. Thus, if a moist soil contains 15 per cent. of water,

specific heat of moist soil

= number of calories required to heat 1 gm. through 1° C.

$= \frac{15}{100}$ gm. water $\times 1 + \frac{85}{100}$ gm. dry soil × sp. ht. of dry soil.

84. Specific Heat of Liquids.—With the exception of water, whose specific heat is taken as 1, we seldom require the specific heat of a liquid. If required it can be determined by the method of mixtures as in Exp. 93, with a piece of metal of known weight and known specific heat, or by various other methods described in text-books on Physics.

85. Specific Heat of Gases.—It is very important to understand the nature of the specific heat of gases in dealing with engines, but we need not discuss it here.

86. Heat Equivalent of Calorimeter.—We have already described one method of determining the heat equivalent (or water equivalent) of a calorimeter, based on the product of its weight and its specific heat. This method, however, does not take into account the heat taken up by the thermometer, stirrer (if used), and packing. The total heat equivalent is easily determined experimentally by pouring a known weight of warm water into the empty cold calorimeter with thermometer, etc., in place, and noting the fall of temperature of the warm water and the consequent rise of temperature of the calorimeter. The usual equation gives the number of calories of heat taken up by the calorimeter, etc., for a rise of temperature of 1°, *i.e.* the water equivalent of the calorimeter.

87. Effects of the High Specific Heat of Water.—The specific heat of water has been found to be much higher than that of the other substances examined. Owing to this, water absorbs much more heat in being warmed than an equal weight of almost any other substance. As a consequence, we find that wet, undrained soils are cooler in sunlight than dry, well drained soils, though they may be warmer in winter when the temperature is too low for growth.

Similarly, near the sea coast the land is warmer than the sea in summer, but owing to the circulation of warmed water from the tropics the sea is generally warmer than the land of the coast in winter. Hence the more general equability of climate of islands and coast lines than of the interior of continents.

CHAPTER VIII.

CHANGE OF STATE : MELTING AND BOILING POINTS : LATENT HEAT : TRANSMISSION OF HEAT.

88. Heat Changes and Changes of State.—Ice when exposed to warm air turns into water, water when heated turns into steam, and so with many other solids and liquids, which, when heated, turn from the solid to the liquid state, and from the liquid state to the gaseous state. Conversely gases can nearly all be turned into liquids by cooling, and liquids into solids.

Hence, in addition to the effects of heating already noted, viz. changes of temperature and changes of size, there are also changes of state to be examined.

The temperature at which a solid changes into a liquid is called its *melting point,* and that at which a liquid boils when the barometer has a height of 760 mm. is called its *boiling point.*

89. Latent Heat.

Exp. 95.—Take three weighed beakers and place in them 100 grams of (*a*) dry ice, (*b*) cold water, and (*c*) nearly boiling water, respectively. Heat the beakers on a sheet of asbestos card or a sand bath, over a Bunsen burner, placing them about equal distances from the flame. Take the temperature of the contents of each beaker every minute as in Exp. 92. Tabulate the results and plot time-temperature graphs as in Art. 78. Also weigh each beaker at the end of the experiment and find the weight of its contents.

Enter your results thus:—

Time in Minutes.	Temperature of Ice.	Temperature of Water.	Temperature of Hot Water.
0	0° C.	19·5° C.	65° C.
1	0°	25·5°	68°
2	0°	31°	70°
3	0°	37°	71·5°
4	0°	42°	73°
5	0°	46·5°	75°
6	0°	51°	76°
7	0°	55·5°	77°
8	0°	59°	78°
9	0°	62·5°	79°
10	0°	66°	80°
11	1°	70°	81°
12	4°	73°	81·5°
13	8°	76°	82°
14	12°	78·5°	82·5°
15	17°	81°	82·5°

We notice that as the three beakers are heated the ice in the first beaker melts, eventually all the ice turns into water, and the water so formed begins to get warm; the cold water in the second beaker becomes hot during the experiment, while the hot water in the third beaker gives off steam, and we find that a considerable quantity of the water has passed off in the form of steam during the experiment. The weights of the first and second beakers show little change.

Fig. 57 shows a time-temperature curve obtained in this experiment. The curve for the ice starts as a horizontal line, the temperature remaining nearly constant (at 0° C.) until most of the ice has melted. After this a regular increase in temperature takes place. The curve for the cold water is nearly straight, showing a regular increase in temperature throughout the experiment. The curve for the hot water starts with an upward slope, parallel to the line for the cold water at the corresponding temperature, but after the water begins to give off steam rapidly the line becomes nearly horizontal, and little

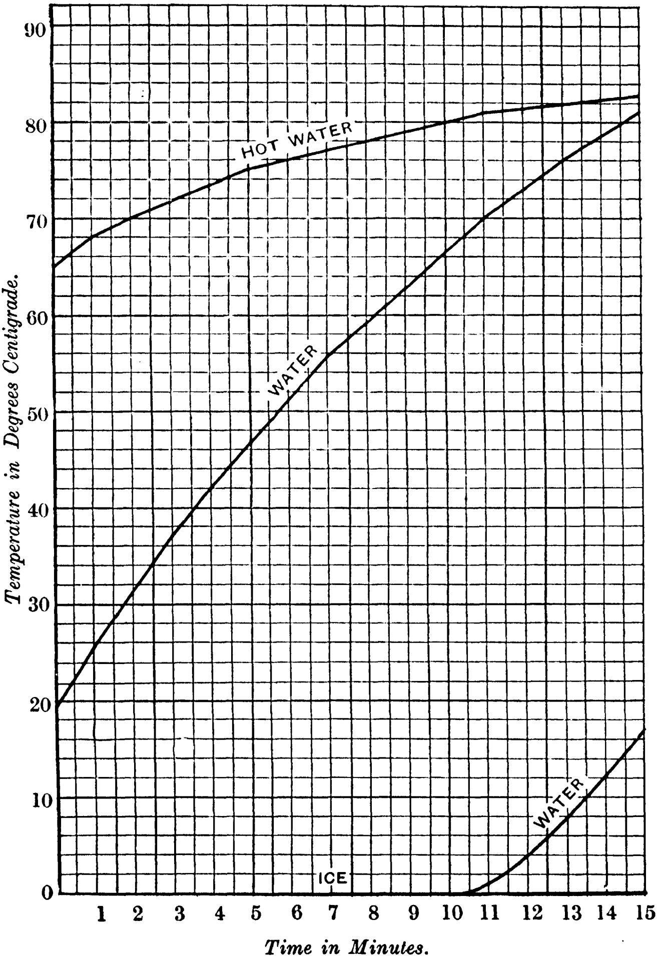
90
80
70
60
50
40
30
20
10
0
HOT WATER
WATER
WATER
ICE
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
Temperature in Degrees Centigrade.
Time in Minutes.

Fig. 57.

further increase of temperature takes place during the remainder of the heating.

We see that while the ice is changing to water and the water to steam there is little increase of temperature, though heat is being supplied to the beakers at a uniform rate all the time, so that the change from solid to liquid or from liquid to gas appears to be accompanied by absorption of heat without any evident rise in temperature. The heat thus absorbed during fusion is called the *latent heat of fusion*, and that absorbed during vaporisation is called the *latent heat of vaporisation.* Corresponding quantities of heat are liberated when liquids solidify or when gases condense to liquids.

We also note that during the melting of the ice the temperature is practically constant, so that this temperature represents the *melting point of ice*, while the similar constant temperature maintained while water is being heated quickly enough to give off bubbles of steam is the *boiling point of water.* (In Exp. 92 the water was not heated to the boiling point.)

Our graph enables us to estimate the quantities of heat required to bring about the changes of state.

Taking first the change from ice to water, we see from Fig. 57 that it has taken 13 minutes to melt the whole of the 100 grams of ice and to raise the temperature of the melted ice to 8°, and that during that time the cold water has risen in temperature from 19·5° to 76°, *i.e.* through 56·5° C. Since the cold water weighs 100 grams, the quantity of heat absorbed $= 100 \times 56{\cdot}5 = 5650$ calories. Since heat is supplied equally to all the beakers, this must be the amount of heat absorbed in melting 100 grams of ice, and in heating the water formed to 8°, which required 800 calories. It therefore requires $\frac{5650 - 800}{100} = 48{\cdot}5$ calories to melt one gram of ice. Another way of expressing this is to say that the latent heat of fusion of ice (sometimes called the latent heat of water) is 48·5 calories per gram.

In the case of the steaming water we found that during 15 minutes of steaming 7·8 grams of water were converted into steam. Now from the curves, during the time the water was steaming the temperature of the water in the second beaker rose from 19·5° to 81° C., so that during this time 100 × 61·5, *i.e.* 6150 calories of heat were supplied to each beaker; this quantity of heat converted 7·8 grams of water into steam, and raised the temperature of the water from 65° to 82·5° C., which required 1750 calories. The quantity of heat required to convert one gram of water into steam is therefore $\frac{6150 - 1750}{7{\cdot}8} = 564$ calories; that is to say, the latent heat of vaporisation of water (or the latent heat of steam) is 564 calories per gram.

90. Determination of Latent Heats.—In Exp. 95 we observed that heat is used in bringing about changes of state, and we found by a simple calculation rough values for the amounts of heat required to convert 1 gram of ice into water at 0° and 1 gram of water into steam at 100°, *i.e.* for the latent heats of fusion of ice and of vaporisation of water. There are many sources of error in the experiment and calculation, some of which might be corrected, but the latent heat can be determined with much greater accuracy by other methods.

91. Latent Heat of Fusion of Ice or Latent Heat of Water.

Exp. 96.—Weigh a calorimeter empty and put into it about 200 gm. of warm water as in Exp. 94. Weigh again, read the temperature of the water, quickly dry a few small lumps of ice with blotting paper, and drop them into the calorimeter. Stir the water with the thermometer and read the temperature as soon as all the ice has melted. Weigh again.

Enter your results as follows :—

Weight of (aluminium) calorimeter = 27·7 gm.
„ „ „ + water = 221·8 gm.
∴ weight of water = 194·1 gm.
Weight of calorimeter + water and ice = 248·8 gm.
∴ Weight of ice = 27·0 gm.
Original temperature of water = 24·4° C.
Final temperature of mixture = 12·1° C.
∴ loss of temperature = 12·3° C.

Now

heat lost by warm water and calorimeter
= heat gained by ice in melting and heat gained by melted ice.

Substituting the numerical values :—

$$194{\cdot}1 \times 12{\cdot}3 + 27{\cdot}7 \times {\cdot}22 \times 12{\cdot}3$$
$$= 27 \times \text{latent heat} + 27 \times 12{\cdot}1$$
$$2387 + 75 = 27\,L + 327$$
$$27\,L = 2135$$

or $$L = \tfrac{2135}{27} = 79{\cdot}1 \text{ calories.}$$

The correct result for the latent heat of water has been found to be nearly 80 calories.

92. Latent Heat of Vaporisation of Water or Latent Heat of Steam.—The latent heat of steam is determined by a method similar to that used in the last experiment, viz. by passing steam at 100° C. into cold water. Just as we find that we get a bad result in Exp. 96 if we use ice which is melting and has water clinging to it (hence the reason for drying the ice with blotting paper) so we find that steam may become condensed into water and carried into the calorimeter. In addition, each bubble of steam which breaks may spray small particles of water into the current of steam which will spoil the result. Water of both kinds is removed by a steam trap.

Exp. 97.—Fit a flask, or better, a tin can, half full of water, with a cork through which are passed a tube bent at right angles and an open safety tube reaching below the surface of the water. Fit up a steam trap as in Fig. 58 by taking a piece of glass tube about 3 in. long and 1 in. in diameter with two corks through which pass two pieces of glass tube not in a straight line and overlapping. Attach one tube to the right-angled tube; the other tube should not be more than about 6 in. long. It is better to wrap the trap in cotton wool and to provide a third tube with jet and pinchcock as shown in Fig. 58 to enable the condensed water to be drawn off from time to time.

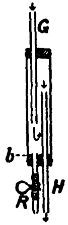

Fig. 58.

Now set the water in the can to boil over a Bunsen flame. Weigh a calorimeter, add about 150 gm. of water and weigh again. Read the temperature of the water. When the water in the can is boiling briskly, raise the calorimeter so that the steam from the trap passes into the water. Stir with the thermometer and read the temperature. As soon as it has risen about

20°, remove the calorimeter quickly, read the temperature carefully, and weigh again.

Enter your results as follows :—

Weight of (aluminium) calorimeter = 22·7 gm.
,, ,, ,, + water = 184·6 ,,
∴ Weight of water = 161·9 ,,
Weight of calorimeter + water + condensed steam = 191·9 ,,
∴ Weight of condensed steam = 7·3 ,,
Temperature of water = 14·4° C.
,, ,, steam = 100° C.
Final temperature = 40° C.

Now

Heat lost by steam in condensing and cooling from 100° to 40° = heat gained by water and calorimeter in rising from 14·4° to 40°.

Substituting the numerical values :—

$$7{\cdot}3 \times \text{latent heat} + 7{\cdot}3 \times 60 = 161{\cdot}9 \times 25{\cdot}6 + 22{\cdot}7 \times {\cdot}22 \times 25{\cdot}6$$

$$7{\cdot}3\,L + 438 = 4145 + 128$$

$$7{\cdot}3\,L = 3835$$

$$L = 525 \text{ calories.}$$

The results of this experiment are subject to various sources of error, due to loss of heat from the calorimeter, gain of heat by the calorimeter from the boiling flask and the flame, and other causes. The former can be lessened by wrapping the calorimeter in dry cotton wool as in Exp. 93, and the latter by putting a screen between the two parts of the apparatus. The correct value for the latent heat of steam has been found to be about 540 calories under ordinary conditions.

93. Effects of Latent Heat in Agriculture.—The high value of the latent heat of water causes the rise of temperature of frozen soil in the spring to be slower than that of dry soil, and it may take some days longer for seeds to grow in the colder soil. Similarly, the loss of water vapour by wet soil requires the latent heat to be supplied, and keeps the soil colder than dry soil. On the other hand, when water is formed from vapour in the air, the latent heat is liberated and the air becomes warmer, as on the west coast of Great Britain, where more rain falls than on the east coast.

94. Melting and Boiling Points.—Curves obtained as in Exp. 95 also enable us to determine with considerable accuracy the melting point of ice if the heating is slow and the boiling point of water if the heating is rapid; these are the temperatures at which the respective curves are horizontal. For the melting point the experiment is often worked the other way by cooling the liquid and finding the point at which the fall of temperature stops for a short time, owing to solidification.

As the melting point of a pure solid and the boiling point of a pure liquid are constant for the same substance, the accurate determination of the melting and of the boiling point is of great assistance in the identification of water and other chemical substances, and may be dealt with here.

95. Determination of Melting Points.—Most solids melt sharply at their melting point, but some, *e.g.* butter, fats, and oils, soften before they melt or become viscous before they solidify. Even in substances of the former class it is sometimes difficult to see the change, as in the change from ice to water. In such cases the melting point can be determined as in Art. 94. When the change is visible the method usually adopted is as follows; this method is suitable for dealing with small quantities.

Exp. 98.—Heat a thin-walled piece of glass tubing in a flame until red hot and draw it off to form a tube of about 1 mm. bore. Cut off a length of about 10 cm. from the tube, and seal one end. Take some crystals of naphthalene and insert a small quantity in the tube, shaking down to the closed end. Place in a small beaker some water or concentrated sulphuric acid, moisten the small tube and stick it against a thermometer so that the solid is about level with the middle of the bulb, as in Fig. 59 (or a small rubber band made by cutting about 1 mm. from a rubber tube may be used). Place the beaker over a small flame, support the thermometer in the liquid and stir. When the white solid suddenly liquefies read the temperature, which is taken as the melting point.

In the cases where there is softening before melting, various methods are used which are studied in analytical work.

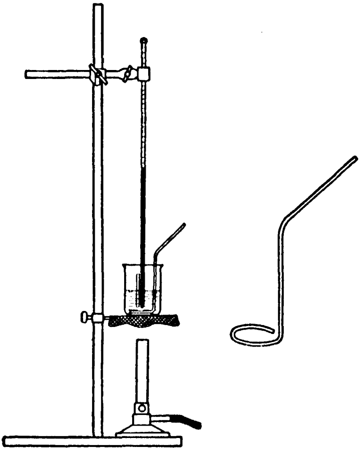

Fig. 59.

96. The Boiling Point.—The boiling point of a liquid does not appear to be so well fixed as the melting point of a solid. When the boiling point of a liquid is determined on a hill it is found to be lower than when determined at sea level, and when determined down a coal mine it is higher than at sea level. It may of course be argued that the boiling point rises with the nearness to the centre of the earth, but while a difference of level of 968 feet causes a rise in the boiling point of water of 1° C., the difference of level is quite negligible as compared with the radius of the earth, about 4,000 miles.

On the other hand, a liquid is only said to boil when the bubbles of vapour formed at the hottest part of the liquid are able to rise and burst at the surface, so that the vapour has the temperature of the boiling point. The conversion of water into vapour involves an expansion of over 1,600 times the volume of the original liquid, so that it would appear to be likely that the pressure of the atmosphere resting on the liquid would cause considerable changes in the boiling point. Every change of 1 mm. in the barometric height would affect the pressure by $\frac{1}{760}$ of an original pressure of 760 mm.

97. Determination of the Boiling Point.—The boiling point is usually determined in a small distilling flask as used to fix the boiling point on an ungraduated thermometer (Art. 56).

Exp. 99.—Fit up a distilling flask as in Fig. 60, placing some alcohol in the flask. The thermometer is adjusted so that its bulb is about 1 cm. below the exit tube. In the case of volatile or inflammable liquids the flask is usually connected with a condenser. Place a flame under the flask and note how the temperature rises, becoming stationary at the boiling point. Read the height of the barometer when the liquid boils; if it stands at 760 mm. the thermometer reading gives the correct boiling point.

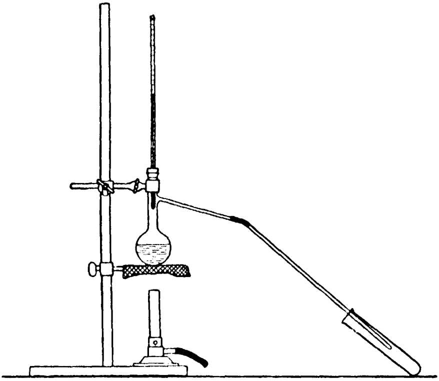

Fig. 60.

98. Change of Volume Accompanying Change of State.—Another change, and one which is important in agriculture, accompanies change of state.

Exp. 100.—Take a 100 c.c. graduated tube, fill it to the 45 c.c. mark with ice-cold water and then put in pieces of dried broken ice until the 100 c.c. mark is reached. Allow the tube to stand until all the ice is melted and read the volume.

It is found that the volume of water is smaller than the volume of ice and water. If the final volume is 95 c.c., then the 55 c.c. of ice only occupy 50 c.c. in the form of water, that is, ice contracts $\frac{5}{55} = \frac{1}{11}$ of its volume in melting to form water. Conversely, water must expand on freezing to form ice.

Exp. 101.—Fill a test-tube with water, cork it tightly, and tie the cork in with string. Put the tube in a freezing mixture of ice and salt.

We note that in a short time the water freezes and bursts the tube, showing the expansion.

This expansion on freezing is of great importance in the cultivation of heavy land, since the water in the ploughed soil expands on freezing and separates the solid clay into crumbs, which can be cultivated and made into a seed bed when the ice melts. The freezing of water in cracks in rocks or in porous building materials also gradually breaks them up. The freezing of water in exposed water pipes may crack the pipe and let the water leak when the ice plug melts.

Some metals likewise expand on solidification, and make sharp castings of the mould into which the molten metal is poured: thus cast iron and steel can both be used for making good castings of many parts of agricultural implements.

On the other hand, some solids expand on melting, so that we cannot make any general rule.

When we boil water in a bottle or flask, large volumes of steam are formed, much larger than the volume of the original liquid. We can calculate the expansion from the density of steam, and the steam is found to have about 1650 times the volume of the water, *i.e.* a cubic inch of water produces about a cubic foot of steam.

99. Curve of Expansion of Water by Heat.—We can now sum up all we have found out about the expansion of water by heat and show the changes in volume from − 10° C. to 110° C. by means of a graph (Fig. 61). The graph given is based on accurate experiments.

We note an increase in the rate of expansion of the water as the temperature rises.

100. Evaporation of Liquids.—It is a common observation that roads and land get dry after a shower of rain, and even in winter a sprinkling of snow or hoar frost gradually disap-

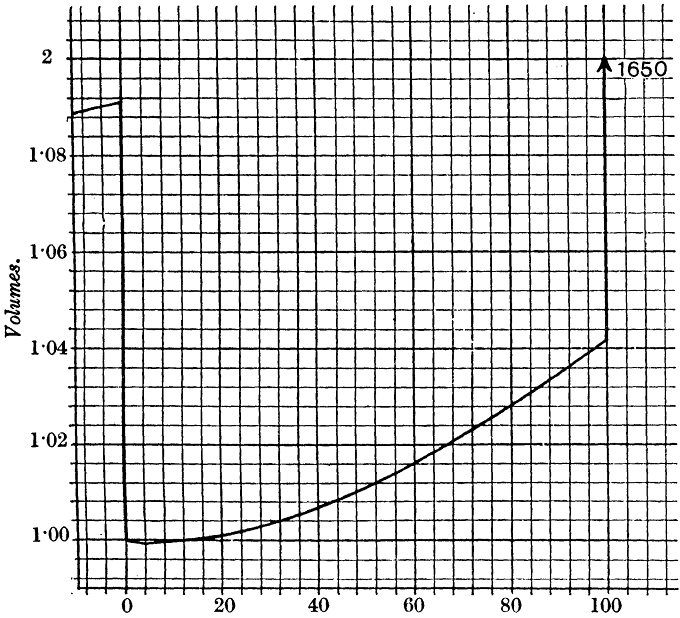

Fig. 61.

pears. Now in both cases the temperature of the road or land is well below the boiling point of water, though we notice that the drying is generally quicker when the weather is warm than when it is cold. Further, in Exp. 95 we found that 7·8 grams of water disappeared in the form of steam at temperatures below 83° C. Again, when the air is cooled, water appears as mist or rain, so that a liquid seems to be able to become a gas without boiling, and to remain in the air well below its own boiling point. A liquid in this state is called a *vapour*, and the change of the liquid (or solid) into vapour below its boiling point is called *evaporation*.

101. Vapour Pressure.—Just as the conversion of water into steam above the boiling point causes a pressure in the containing vessel, so water exerts a pressure in evaporating below its boiling point.

Exp. 102.—Fit up a barometer tube *B* (Fig. 62). Gum a narrow strip of paper on the side of the tube and mark on it the present level of the mercury surface. Suck a quantity of water into the curved pipette (Fig. 63), and, placing the end *C* under the barometer tube, release a drop of water: the drop, being lighter than mercury, will at once rise to the top of the mercury; it will then evaporate readily and disappear. Measure any change in the height of the mercury column; introduce a few more drops of water, and measure the change again.

Repeat the experiment, using a fresh barometer tube, and passing alcohol, or better, ether into the tube.

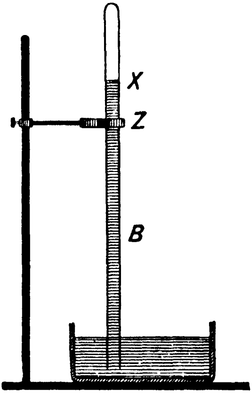

Fig. 62.

It is noticed that the first drops of liquid that are added disappear, and that the column of mercury becomes lower. Now we know that the column of mercury is held up by the pressure of the air on the surface of the mercury in the vessel, so that any lowering of the column must be caused by a pressure on the surface of the mercury inside the tube, that is, by a pressure exerted by the liquid when it evaporates.

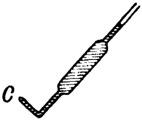

Fig. 63.

It is further seen that after the addition of a certain quantity of the liquid it no longer all disappears but is partly left floating on the mercury. When this takes place, the further addition of liquid does not affect the height of the column, unless enough is added to depress the column by its own weight. At this stage the space and the vapour are said to be *saturated*, and the depression of the mercury column is said to be the *vapour pressure* of the liquid. It is noted that the vapour pressure of water in the laboratory is about 12-15 mm., while that of alcohol is about 30-40 mm., and of ether about 350-400 mm.

Exp. 103.—Repeat Exp. 102 using a barometer tube into which dry air or any other gas has been passed until the mercury column is lowered about half way.

The same phenomena are observed, so that both evaporation and the vapour pressure produced are independent of the contents of the space.

On a hot day the vapour pressure is found to be higher than on a cold day.

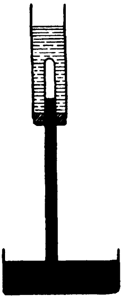

Fig. 64.

Exp. 104.—Take a wide tube fitted at the lower end with a cork or rubber stopper bored to fit the barometer tube, and pass it over the upper end of that tube (Fig. 64). Pour into the wider tube water at 30° C., and proceed as in Exp. 102, introducing liquid into the vacuum until the space is saturated. Read the temperature and measure the vapour pressure. Pour water at a higher temperature into the wide tube, stirring well, until the temperature is about 35° C. Measure the vapour pressure again. Repeat at higher temperatures.

We notice that as the temperature rises more water evaporates and the vapour pressure increases, and if we carry on the experiment until the boiling point is reached the vapour pressure is equal to the atmospheric pressure.*

We can hence define the boiling point of a liquid as the temperature at which the *vapour pressure is equal to* 760 *mm.*, i.e. *to the pressure of the atmosphere under standard conditions.*

102. Effect of Vapour Pressure on the Measurement of Gas Volumes.—We have seen in Exp. 103 that the pressure of the vapour of water mixed with a gas causes the volume to become larger. Now a gas given off in a chemical reaction is generally collected over water, and becomes saturated with water vapour. Also in measuring the volume of breath we have to remember that it too is saturated with water vapour. We can allow for the effect in the formula we have already found for determining the volume of any gas at 0° C. and 760 mm. pressure (see Art. 61), if we consider that the pressure of the gas + the pressure of the water vapour = the pressure of the atmosphere. Our final correction formula thus becomes

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* Other methods of showing this are more convenient and are described in all text-books of Physics.

$$\frac{VP}{t+273} = \frac{V'(\text{press. of atmos.} - \text{vap. press. of water at } t'^{\circ})}{t'+273},$$

when the water is levelled inside and outside the measuring tube before the volume is read.

103. Transmission of Heat.—The growth and ripening of our crops and the changes which take place in the soil require the maintenance of a minimum temperature during the growing season. The heat required for this purpose (except in the case of warm glass-house work) is derived from the sun, and passes through 92 millions of miles of space before it reaches the earth. The heat required for heating a glass-house is mostly derived from burning carbon.

The maintenance of animal life also requires that the body should be kept at a definite temperature in spite of losses in the breath and from the skin. The heat required for the purpose is mainly derived from the oxidation of our muscular substance in a special way, and is carried about the body by the blood in the blood vessels, which are in contact with nearly all the body tissues.

Three main ways in which heat passes from hot to cold bodies and vice versa are generally distinguished, viz. :—*radiation*, *conduction*, and *convection*.

104. Radiation.—The transmission of heat from the sun to the earth is perhaps the most important case of *radiation*. The sun is an immense body at an enormous temperature, much hotter than anything we know on the earth. The temperature of the space between the sun and the earth, however, is very low, probably not far removed from — 273° C., in spite of the radiation from the sun which is continually passing through it, while the sun's rays, after passing through the 92 million miles of space between sun and earth, heat the earth's surface.

It appears, therefore, that a characteristic of the transmission of heat by radiation is that radiant heat can pass through space without much loss and without heating the space, until it reaches a surface which absorbs the radiation and consequently becomes warmed.

Every body radiates heat, but some receive more than they give out and become warmer, while some give out more than they receive and become colder. The radiation and absorption of heat by a body depend in practice on certain facts and relationships :—(i) heat and light are closely related and can be converted the one into the other, (ii) a good radiator or absorber of heat may have different characters as regards light, (iii) a body which radiates heat easily also absorbs heat easily, while one which radiates badly is also a poor absorber.

We have many examples illustrating these facts; thus a polished metallic surface absorbs heat slowly and radiates it slowly, and so cools slowly, while a dull or rough surface cools and warms more quickly. Another effect is seen in the absorption of heat and light by green leaves, so that the soil under green trees or a green crop does not get so warm as bare soil. Similarly, a dark soil or soil covered with soot gets much hotter in sunshine than a light chalky soil or soil with white stones, since a black surface absorbs light better than a white one.

Further, we find that some substances are transparent to light but opaque to dark invisible heat, such as is given off from boiling water or warm soil. This property is put to most practical use in the case of glass, which allows light to pass through but not dark heat. When, therefore, the sun has been shining on a glass-house, the inside soil and staging become heated by the light; after dark, the dark heat from the soil is radiated but cannot pass quickly out through the glass into the colder space outside. Hence the interior of the house remains warm.

A somewhat similar effect is seen in the case of light and dark soils, which in the dark lose heat at much the same rate, though the dark soils absorb light better than the light ones.

105. Conduction.—When a piece of metal is heated at one end or in one place, the surrounding metal rises in temperature, but the part nearer the heater is always hotter than the part further from the heater. Heat carried in this way is said to be *conducted*, and the characteristics of conduction differ from those of radiation in that there is always a gradual fall of temperature between the hot source and the part heated by conduction.

Different bodies differ in their power of conducting heat; thus if a copper rod and an iron rod of equal size are both held in a similar position in the same flame the copper rod becomes much hotter than the iron rod at an equal distance from the flame.

Where we want to be able to handle hot bodies, as in forging or soldering, they are generally held by iron tools or handles, and where we want heat to pass rapidly through a plate, as in a kettle or steam boiler, we get the best results by using a copper bottom, firebox, or tubes. In cooling milk, too, we make use of cold water running in copper tubes.

Substances such as wood, glass-wool, cotton-wool, and asbestos are bad conductors of heat, and are generally used as coatings where we wish to prevent loss of heat from hot bodies such as steam boilers.

106. Convection.—In the third common method of transmitting heat, by *convection*, the heat is carried from a hot place to a cold one by the actual movement of some liquid or gas. The motion may be mechanical, as in the movement of blood by the pumping action of the heart, or in the movement of the ocean currents and wind streams by the motion of the earth. More generally the movement is caused by the action of heat upon the volume and density of the conveying substance.

Exp. 105.—Place a large beaker nearly full of water on a tripod stand and put a small flame under one side. Drop a crystal of potassium permanganate or some sawdust into the water above the flame and note what happens.

We observe that the heated water above the flame rises, overflows across the top of the cold water and down the other side. This is explained by the expansion of the heated water, which is immediately driven upward by the cooler and denser water, thus causing a circulation by which the heated water carries the heat away from the flame and gives it up on its course. The principle is used in hot water heating apparatus.

The case of gases is exactly similar, but not so easy to observe. It can, however, be observed in a beaker about half full of nitrous fumes (Exp. 4) and well covered with a clock glass.

Convection currents in the atmosphere and in the sea are set up in the tropics by the heating of air and water by the sun, and are helped in the former case by the formation of large quantities of water vapour : as we have already noted, the water vapour is condensed in the form of rain when the air becomes cooled in its course towards the poles, and the latent heat of the water vapour is liberated. Such deposition of rain, with accompanying liberation of heat, takes place on the western shores of Europe.

107. Condensation of Water Vapour contained in the Atmosphere.—Since any volume of air saturated at any temperature will require less water vapour to saturate it at a lower temperature, any excess must be deposited when saturated air is cooled. If the air is only cooled slightly below saturation point we find the deposit taking the form of mist or fog ; the thickness of the fog depends on the amount of water vapour in the air cooled and the amount of cooling. Greater cooling produces rain or snow.

108. Formation of Dew and Hoar Frost.—A considerable quantity of water is deposited in the course of a year upon the surface of the land and of plants in the form of dew and hoar frost. When the land cools on a clear night by radiation, it cools the air touching it, and may cool it so much that the water vapour it contains becomes more than sufficient to saturate it. The air then deposits any excess of water in the form of dew, or, if the temperature is below freezing point, of hoar frost.

The blades of grass and the leaves of trees, being light, get cold more quickly than a bare land surface, so that more dew appears on vegetation than on soil. Again, clouds prevent rapid radiation and so prevent the formation of dew. Very gentle motion of the air over the cold surfaces allows a larger volume of air to be cooled and consequently more dew to be formed, while a wind may move the air over the cold leaves so rapidly that it never gets cooled to saturation point, and so no dew is formed.

CHAPTER IX.

DIFFUSION OF GASES: THE MOLECULE: EQUIVALENTS.

109. The Diffusion of Gases.—We have now examined four gases, oxygen, nitrogen, carbon dioxide, and hydrogen, and the only striking difference between them which we have observed without applying any chemical tests is in their densities. We may now try to ascertain whether there are any other important physical differences.

Exp. 106.—Fill a cylinder with carbon dioxide. Stand it on the bench and remove its lid. Test the gas every five minutes with a burning taper, and note each time the appearance and the position of the surface of the gas.

Perform a similar experiment with a test-tube of hydrogen supported mouth downwards in a clamp and filled by displacement, testing at intervals of ½, 1, 1½, 2, . . . minutes after filling the tube, which must be refilled after each test. Note the effect.

We note that the surfaces separating the gases and the air are invisible, and that the gases appear to be able to pass out of, and the air to pass into, the cylinders against the force of gravity.

Exp. 107.—Place a lump of carbonate of ammonia or a few c.c. of liquor ammonia on the bench, and note the distance at which it can be smelt in various directions.

Nothing can be seen to be given off, or to be present in the air, yet ammonia may be smelt at a distance of some feet in every direction.

The process by which gases pass from one point to another by themselves is termed *diffusion*, and the fact that gases diffuse shows that they are in motion of some kind.

Exp. 108.—Take a round pot of porous porcelain such as is used in a galvanic battery, and fit it with a well-fitting cork through which passes a straight glass tube of, say, 5 mm. bore and about 50 cm. long. The other end of the glass tube is passed through a cork bored with two holes, which is fitted into a wide-mouthed glass bottle, and through the other hole of the cork is passed a piece of glass tube bent at right angles, and drawn out to a fine point. The bent tube should reach nearly to the bottom of the bottle, which is partly filled with water coloured by red or black ink, and the straight tube should just pass into the bottle. Place the pot by the fire, or in an oven, till dry and warm, and fill a bell jar with hydrogen. Then fix the pot tightly on its cork, carefully raise the bell jar, and lower it over the pot (Fig. 65). After a short time remove the bell jar. Note any indications of movement of the gases.

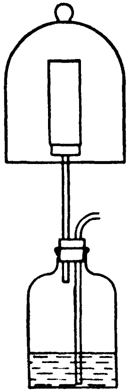

Fig. 65.

We note that bubbles at once pass out of the pot into the bottle, and that the liquid is expelled from the jet. It is evident that something must have passed into the pot and expelled air, and the only thing present round the pot is the hydrogen. On removing the bell jar we notice that bubbles run from outside into the bottle; this confirms our inference that hydrogen is able to pass through a porous pot into air.

Why should the movement of the hydrogen cause a change of volume and corresponding change of pressure in the contents of the porous pot? This is most likely because the hydrogen can get in more quickly than air can get out. Now hydrogen is lighter than air, so we ought to examine another gas of different density, say carbon dioxide.

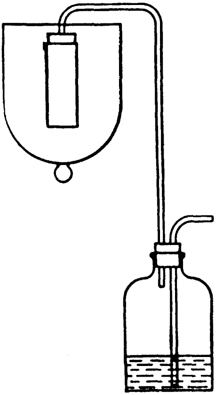

Fig. 66.

Exp. 109.—Repeat Exp. 109, but bend the tube passing into the porous pot twice at right angles (Fig. 66.) Fill the bell jar with carbon dioxide, and raise it until the pot is immersed in the gas.

We note a movement of air out of the porous pot, causing bubbles to run into the bottle, and when the bell jar is removed there is an increase of pressure inside the porous pot, showing that air can pass through the porous pot more quickly than the carbon dioxide can.

From these experiments it appears that hydrogen moves more quickly than air, and air more quickly than carbon dioxide. We can make the general statement that the lighter a gas is the more quickly it can pass into or out of a space filled with some other gas, either when free or when contained in a vessel with very small holes in its walls.

It has been found that the rates of diffusion of gases are connected by this Law :—Gases diffuse at rates which are inversely proportionate to the square roots of their densities.

110. Solution of Gases.—We have seen in Exp. 89 that water dissolves air which can be driven out by boiling, *i.e.* a gas can pass into or out of a liquid.

Exp. 110.—Boil some water, allow it to cool, and place it in a crystallising pan after testing some of it with lime-water. Fill a jar with carbon dioxide, and invert it over the water. Note the position of the water in the jar from time to time. When the water has stopped rising, test it with lime-water.

We not only confirm the fact that a gas can be dissolved by a liquid, but we also note that the gas can pass into the liquid of its own accord, through the surface of the liquid and without being shaken with it.

111. Molecules. Avogadro's Law.—These facts are best explained by the assumption that all substances are built up of small, very small, particles called **molecules**, in a state of motion. A molecule may be defined as *the smallest portion of any chemical substance capable of a free and independent existence.* This definition does not mean that a molecule is the smallest particle of matter which can exist, but only that if a molecule can be divided up it loses its characteristic chemical properties.

The molecules of any substance cannot be packed tightly enough, even in a solid, to leave no spaces between them, and into these spaces the molecules of gases can insert themselves. We can distinguish between a liquid and a gas by considering that at the free surface the molecules in both cases are free to, and do, move. In the case of a gas, many molecules are able to get away from the main body of the gas, while in a liquid the greater number of molecules are moving more slowly and are confined by the surface, through which comparatively few molecules can pass off at temperatures below the boiling point of the liquid.

Now all gases obey the Laws of Boyle and Charles (Chap. V., Arts. 60 and 61), which suggests that they resemble one another in some other respect. Also we noted that hydrogen and oxygen combined in the ratio of 2 c.c. to 1 c.c. to form 2 c.c. of steam. An explanation of the resemblance can be deduced mathematically to explain the observed facts, and the explanation is that the number of molecules in a constant volume of all gases is the same, under similar conditions ; it is usually expressed as a Law, **Avogadro's Law.**

This most important law can be stated thus :—

Equal volumes of all gases under the same conditions of temperature and pressure contain equal numbers of molecules.

112. Molecular Weights.—By the use of Avogadro's Law we can find the weights of the molecules of different gases, since if d is the density of any gas, m the weight of a molecule, and n the number of molecules in 1 c.c., then $d = nm$ and $m = \frac{d}{n}$.

Unfortunately for this unit, n is very large, being, in the case of hydrogen, in the neighbourhood of

50000,000000,000000 at 0° and 760 mm.,

so that the weight of a molecule is too small to be used conveniently. We can, however, by another use of Avogadro's Law, obtain a method of comparing the weights of the molecules of two gases, that is we can find their *relative molecular weights*. Thus :—

If m_1, m_2 are the weights of the molecules of two gases, if d_1, d_2 are the corresponding densities, and if the densities d_1

and d_2 are determined at the same temperature and pressure, then the number of molecules in 1 c.c. of each gas is the same $= n$, and

$$d_1 = nm_1 \text{ and } d_2 = nm_2.$$

Dividing, we obtain $\frac{d_1}{d_2} = \frac{nm_1}{nm_2} = \frac{m_1}{m_2}$.

That is :—

Under the same conditions of temperature and pressure the weights of the molecules of all gases are proportionate to the densities of the gases.

By selecting a standard molecule as our unit we can express the weights of all other molecules in terms of that unit, and we have selected as our unit the weight of the molecule of the lightest gas known to us, viz. hydrogen. This unit, for reasons which we shall see later, has been taken as 2, and the ratios of the weights of the molecules of other gases to that of hydrogen taken as 2 are called the *molecular weights* of the gases. It must, however, not be forgotten that the molecular weight of a gas is not the weight of its molecule, but the ratio of this weight to that of the molecule of hydrogen taken as 2.

If we make the weight of the molecule of hydrogen equal to 2 in order to avoid small decimals, we must agree upon a standard of densities which will make them also of a similar order. This is done by making our standard density that of hydrogen (1 c.c. $= 0{\cdot}00009$ gm.) taken as unity, so that the relationship of the molecular weight to density on this standard is

$$m = 2d = \frac{2 \times \text{weight of 1 c.c. of vapour}}{0{\cdot}00009},$$

or *the molecular weight of any gas on the scale in which hydrogen is taken as* 2 *is represented by twice its density on the scale in which hydrogen is taken as* 1.

Densities on this scale (H = 1) are very generally called *vapour densities.* Applying this rule to the densities of oxygen, nitrogen, carbon dioxide and steam, which we have already found, we obtain :—

$$\text{Molecular weight of oxygen} = \frac{2 \times \cdot00143}{\cdot00009} = 32.$$

$$\text{,, ,, ,, nitrogen} = \frac{2 \times \cdot00125}{\cdot00009} = 28.$$

$$\text{,, ,, ,, carbon dioxide} = \frac{2 \times \cdot0198}{\cdot00009} = 44.$$

$$\text{,, ,, ,, steam} = \frac{2 \times \cdot00082}{\cdot00009} = 18.$$

113. Effects of Diffusion of Gases.—In everyday life the diffusion of gases is of great importance to living bodies. Air passes into the lungs on inspiration and the oxygen diffuses into and is absorbed by the blood, while carbon dioxide diffuses from the blood into the air and is removed on expiration. The carbon dioxide mixes with the external air by diffusion, and will pass through brick walls or roofs ; oxygen passes in as removed, thus helping in ventilation. A similar but reversed exchange takes place in green plants.

114. The Composition of Water by Weight.—It is now necessary to find the composition of some molecules by weight, and for that purpose we may start with the determination of the composition by weight of water. This determination also serves to illustrate the care and precautions which must be taken to ensure accurate results in chemical work. There are at the start difficulties in weighing oxygen, hydrogen, and water with accuracy, but if we can find a method of weighing two of them accurately, we can obtain the third by subtraction.

Exp. 111.—Take a piece of combustion tube about 20 cm. long, and fit each end with a singly bored cork and glass tube. Fill the tube with bright copper turnings or a roll of copper gauze. Heat the copper and pass over it some oxygen prepared as in Exp. 30. Note any change. Now fit up an apparatus for preparing hydrogen as in Exp. 75. Pass the gas over the copper oxide until all the air is expelled ; then warm the copper oxide. Note the changes and test the liquid product.

We note that the copper first becomes black by combination with oxygen, forming copper oxide (a process of oxidation). The oxide is then converted into metallic copper by the hydrogen, and water is formed. The removal of oxygen from an oxide is called a *reduction* of the oxide and is the reversal of the process of oxidation. If, in the above experiment, we weigh the copper oxide before and after heating it, the difference between the weights is that of the oxygen used; and if we collect and weigh the water formed, the difference between that weight and the weight of oxygen is the weight of hydrogen used.

It is necessary to be very careful to use pure materials, and also to dry the hydrogen gas very thoroughly.

Exp. 112.—Fit up an apparatus for preparing pure hydrogen, using fairly pure zinc and dilute pure sulphuric acid. Pass the gas through a series of U-tubes filled with potash solution (*a*), sticks of potash (*b*), and pumice moistened with pure concentrated sulphuric acid (*c*). Place the copper oxide to be weighed in a tube (*d*) made by drawing out a piece of combustion tubing 1 cm. or so in bore and 15 cm. long, in such a way as to leave 6 or 7 cm. of the original tube with a narrower piece at each end of about the same length. Put a small piece of loose asbestos in to form a plug, then fill with pure granulated copper oxide, and lastly put in a little more loose asbestos. Before the tube can be used it must be heated to a red heat and air blown through, and while hot the ends must be carefully closed by short caps of rubber tube (2 cm.) fitted with short pieces of glass rod. The water is weighed in one or two tubes filled with calcium chloride (*e*), and capped like the copper oxide tube (Fig. 67). First weigh the copper oxide tube and the calcium chloride tube with their caps on. Then connect up the apparatus, keeping the caps distinct, expel all the air by the hydrogen, testing for the presence of air as in Exp. 75, warm

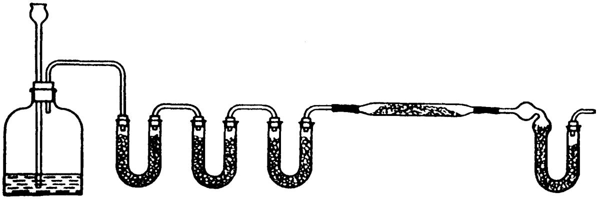

Fig. 67.

the copper oxide tube, and allow the hydrogen to pass until all the water formed is carried over into the calcium chloride tube. Disconnect, replace the caps on their right tubes, cool, and weigh again.

To take an example :—

Weight of copper oxide tube (before) = 20·421 gm.
,, ,, ,, (after) = 19·380 gm.
,, ,, oxygen used = 1·041 gm.
Weight of calcium chloride tube (after) = 38·485 gm.
,, ,, ,, (before) = 37·305 gm.
,, ,, water formed = 1·180 gm.

Now find the weight of the hydrogen by subtraction, and calculate the percentage composition thus :—

Water = 1·180
Oxygen = 1·041
Hydrogen = 0·139
or Oxygen = 1·041 = 88·2 %
Hydrogen = ·139 = 11·8 %
Water = 1·180 = 100·0

115. Equivalents and their Determination.—It is found, when the composition of water by weight is very carefully determined, that it is perfectly fixed and obeys the Law of Definite Proportions, so that each weight of either element may be said to be *equivalent* to the other, *i.e.* 11·1 gm. of hydrogen are equivalent to 88·9 gm. of oxygen. (This is the correct value, that given above being an ordinary experimental value.)

If the copper oxide tube is weighed before the copper oxide is put in, we can determine the weight of copper which is equivalent to the other two elements. Thus if the weight of the copper oxide tube empty is 15·27 gm. then the weight of copper oxide taken = 20·42 – 15·27 = 5·15 gm., and the weight of copper left = 19·38 – 15·27 = 4·11 gm., so that since the 1·04 gm. of oxygen were originally combined with 4·11 gm. of copper, these two weights must be equivalent, and also equivalent to 0·139 gm. of hydrogen.

Now when we have a series of ratios of this kind which are related, it is usual to take one of the numbers as a standard and define the others from it. The standard originally adopted was that of hydrogen taken as unity. Using this standard the numbers become :—

Hydrogen = 1.
Oxygen = 8.
Copper = 31·5.

Since oxygen combines with more substances than does hydrogen and the most accurate determinations have shown that $H : O = 1{\cdot}008 : 8$, it is more correct to make our definition thus :—

An *equivalent* (*equivalent weight*) of an element is the weight of that element which will combine with or replace 8 gm. of oxygen. 31·5 is therefore an equivalent weight of copper.

Since the molecular weight of a gas $= 2d$ $(H = 1)$,

$$\text{mol. wt.} = 2 \times \frac{\text{wt. of 1 c.c. of the gas}}{\cdot 00009} = 2 \times 11100 \times \text{wt. of 1 c.c.}$$

$$= \text{wt. of 22200 c.c. or } 22{\cdot}2 \text{ litres of the gas.}$$

If, however, we adopt the value 8 for the equivalent of oxygen this figure must be corrected by the fraction $\frac{1{\cdot}008}{1{\cdot}000}$ and

mol. wt. of a gas = wt. of 22·4 litres at 0° C. and 760 mm.

We can also determine equivalents of other elements by making use of the fact that they displace hydrogen from dilute acids.

Exp. 113.—Weigh out 0·1 gm. of magnesium wire or ribbon, fold it up, and place it in a small test-tube about 4 cm. long, which is then filled with water. Now take a straight eudiometer tube, to hold 100 c.c., and fill it with dilute hydrochloric acid; invert it in a basin or crystallising pan containing water, and quickly pass the little test-tube containing the magnesium into it. If the little tube is placed mouth downwards in the crystallising pan and then inserted into the eudiometer, mouth upwards, no loss of gas will be noticed (Fig. 68). The magnesium dissolves and rises in the tube: when all the magnesium is dissolved, level the water inside and out of the tube as in Exp. 36, and measure the hydrogen, taking its temperature and the pressure of the atmosphere.

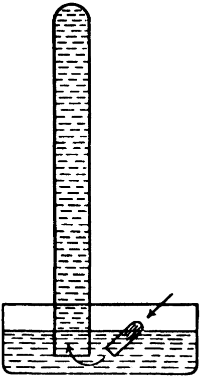

Fig. 68.

Correct for temperature and pressure, and calculate the weight of the hydrogen; 1 c.c. of hydrogen at 0° and 760 mm. weighs ·00009 gm. Calculate now the weight of magnesium required to displace 1 gm. of hydrogen: this is the equivalent of magnesium.

Exp. 114.—Repeat the above experiment, using zinc foil instead of magnesium, and calculate as before. (Iron, aluminium, and tin may also be used, but if tin is examined use a basin instead of a crystallising pan, placing it on a tripod and heating it, and use also more concentrated hydrochloric acid).

CHAPTER X.

COMMON SALT: HYDROCHLORIC ACID: CHLORINE. THE ATOM: ATOMIC WEIGHTS: EQUATIONS.

116. The Examination of Salt.—Common salt is obtained by the evaporation of sea water or brine springs, or in the form of *rock salt* by mining.

Exp. 115.—Take a lump of rock salt and heat it. Note its behaviour and its effect on the flame. See if it dissolves when shaken with water, by evaporating a little of the liquid on a watch glass after filtering it.

We find that rock salt is a soluble solid, colourless when pure. It melts when heated and turns the flame yellow, but is apparently unchanged.

117. The Preparation and Properties of Hydrochloric Acid Gas.

Exp. 116.—Take a gas jar and place some salt in the bottom, pour on it some strong sulphuric acid, and cover the jar with a glass plate (Fig. 24). Note whether any reaction takes place and the character of the products. When the cylinder is apparently clear, remove the plate. Note whether the gas remains in the jar, and the character of its fumes. Plunge a lighted taper into the jar; note the effect.

Pour the gas downwards from the jar into another dry jar, and pour a few drops of water into it: shake the jar, and in a few seconds try the effect of lowering a lighted taper again. Taste a very small quantity of the liquid. Test the liquid by adding a solution of litmus and by adding a few drops of a solution of nitrate of silver followed by ammonia solution.

As the gas appears to be soluble in water, repeat the experiment and fill another dry jar. Cover it with a piece of stiff paper, and invert it in a bowl of water. Note the effect.

[*Note.*—The gas can also be prepared as in the next experiment, and collected by downward displacement in the same way as carbon dioxide.]

By the action of sulphuric acid on salt we have prepared a new gas, which is colourless, fuming, and has a pungent smell. It is heavier than air, very soluble in water, turns litmus red, and puts out a burning taper. It also gives white fumes with ammonia gas, and a white precipitate, soluble in ammonia, with silver nitrate solution. From its source it is termed *spirit of salt*, or generally *hydrochloric acid gas*.

118. The Preparation of Hydrochloric Acid Solution. Nature of Acids.

—As the gas is soluble in water, we may prepare a quantity of the solution.

Exp. 117.—Take an 8 oz. flask, put into it some lumps of common salt, and fit it with a cork bored with two holes, through which pass a thistle funnel and a tube, bent twice at right angles, to the free end of which the tube of a funnel is attached by means of a piece of indiarubber tube (Fig. 69).

Support the flask in a clamp and place the funnel in a beaker, adding water till it only just touches the rim of the funnel. Now pour sulphuric acid into the flask, and warm gently until a considerable quantity of the gas given off is absorbed by the water in the beaker. Examine the solution thus prepared. Test with litmus, zinc, and chalk, and note the effects.

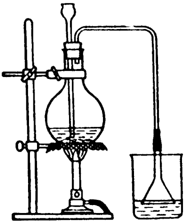

Fig. 69.

We note that the litmus is turned red, the zinc displaces hydrogen, and the chalk gives off carbon dioxide.

A solution or liquid which turns litmus red, dissolves metals setting free hydrogen, and decomposes carbonates is termed an *acid*, and this solution of hydrochloric acid gas is called commercially *muriatic acid, spirits of salt*, or, more generally, *hydrochloric acid.*

Exp. 118.—Take a test-tube and put into it a small quantity of the red oxide of lead. Pour into it some strong solution of hydrochloric acid, and note the effects. Boil until the contents are colourless, being careful not to inhale any fumes, and allow to cool slowly; note the appearance.

Hydrochloric acid appears to react with red oxide of lead, giving a white crystalline solid soluble in hot water and crystallising out on cooling; a yellowish gas with a characteristic smell is also given off. Hence it is not unlikely that hydrochloric acid is either a mixture or a compound which can be split up into hydrogen, this yellow gas, and possibly other substances; we may, therefore, try the effect of metals and of red lead on hydrochloric acid gas itself.

119. The Decomposition of Hydrochloric Acid Gas.

Exp. 119.—Take a piece of combustion tube about 20 cm. long, and fit the ends with corks through one of which passes a short piece of glass tube, and through the other a tube for collecting a gas over water. Half fill the combustion tube with granulated zinc, and arrange it horizontally with the delivery tube under water. Now attach to the short piece by means of an indiarubber tube the hydrochloric apparatus used in Exp. 117, but having as its delivery tube a simple bend at right angles (Fig. 70).

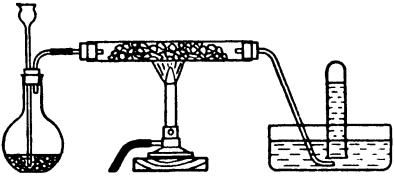

Fig. 70.

Pass the gas over the zinc, warming it if necessary. Collect the gas coming through the tube in a test-tube and note whether it is soluble, after throwing away the air which passes over first. Test the gas which comes over with a taper. Note any changes in the zinc.

From this experiment we observe that hydrochloric acid gas which is free from water (since it is given off from strong sulphuric acid) is yet able to yield a light gas when it reacts with the element zinc. This light gas burns in air and is hydrogen; the hydrogen must be contained in the gas, in chemical combination.

Exp. 120.—Repeat the preceding experiment, placing red lead oxide in the combustion tube instead of zinc. Note the colour of the gas collected and test it with litmus. Test if it is heavier than air.

We note that hydrochloric acid gas reacts with red lead, giving a yellow heavy gas with a powerful smell, which bleaches litmus.

On account of its colour, this gas is called *chlorine* (symbol = Cl).

Since red oxide of lead gives off oxygen when heated alone we may infer that the preparation of chlorine requires the presence of oxygen. It is probable that the chlorine is prepared from the hydrochloric acid by oxidation, so that we may be able to make use of other substances as well as the red oxide of lead for its preparation.

120. The Preparation and Properties of Chlorine.

Exp. 121.—(*To be done in the draught chamber or out of doors.*) Put in test-tubes (i) some manganese dioxide and hydrochloric acid, (ii) some potassium permanganate and hydrochloric acid. Note the reaction in the latter case. Warm the former and note what takes place. Now place in another test-tube (iii) some salt and manganese dioxide, pour on some strong sulphuric acid, and warm : note the change.

We note that potassium permanganate sets free chlorine in the cold, that manganese dioxide does so on warming, and that it is not necessary to prepare hydrochloric acid first, since the mixture of salt and sulphuric acid acts in exactly the same way as the free acid.

Exp. 122.—(*To be done in the draught chamber or out of doors.*) Place about 3 gm. of potassium permanganate in each of six gas jars and cover them with glass plates. Pour down the side of each jar enough hydrochloric acid to cover the crystals, replace the covers and allow the jars to stand until full of chlorine. Into (i) plunge a burning taper, (ii) sprinkle some finely-powdered antimony, (iii) lower a piece of phosphorus on a deflagrating spoon, (iv) place an old envelope with postmark and stamp, also a piece of coloured cloth well dried beforehand, (v) place two or three drops of turpentine on a warmed filter paper. Pour the gas from (vi) into another dry jar, put in some water and shake ; note whether the gas is heavy or light, and soluble or insoluble in water.

Chlorine is seen to be a very heavy yellow gas, soluble in water to some extent, which allows a taper to burn with a smoky flame and causes antimony, phosphorus, and warm turpentine to burn. It also bleaches vegetable colours (but not printers' ink) when moist, and not when dry. We must discuss the explanation of these reactions later.

***Exp. 123.**—(*Demonstration Exp.*) Determine the density of chlorine as in Exp. 53. Prepare the chlorine in a flask fitted with a thistle funnel and delivery tube for collecting by downward displacement, by pouring concentrated hydrochloric acid on potassium permanganate crystals. Calculate the weight of 22·4 litres of the gas.

We find that the weight of 22·4 litres of chlorine is 71 gm., and as we have decided that this weight represents the molecular weight of a gas, taking hydrogen as the standard (= 2) or, better, oxygen (= 32), then the molecular weight of chlorine = 71.

121. The Composition of Hydrochloric Acid Gas and the Molecule of Hydrogen.—We can now discuss the relationship between the chlorine, the hydrogen, and the hydrochloric acid gas from which they are apparently derived.

Exp. 124.—(*To be done in the draught chamber.*) Prepare a jar of chlorine as in Exp. 122. Set up a hydrogen apparatus with a tobacco pipe jet as in Exp. 77, light the hydrogen *when free from air,* and lower it into the jar of chlorine. Note the reaction.

Hydrogen and chlorine combine under the influence of heat to form a colourless, fuming gas, probably hydrochloric acid. We can confirm this inference by examining the effect of passing an electric current through a concentrated solution of the gas, when we find that hydrogen and chlorine are, after some time, given off in approximately equal volumes.

In Exp. 81, we noted that dilute hydrochloric acid is decomposed by the electric current into hydrogen and oxygen, and we decided that it must be the water which was decomposed, so that it seems probable that the substance which is decomposed in this case, yielding hydrogen and chlorine in equal volumes, must be hydrochloric acid, and this is confirmed by other experiments.

Further, hydrochloric acid gas is decomposed by metals and the hydrogen left occupies half the volume of the original gas. Since the hydrogen and chlorine volumes are equal, the gas must also contain half its volume of chlorine. In other words, 2 c.c. of hydrochloric acid gas are built up of 1 c.c. of hydrogen and 1 c.c. of chlorine.

Applying Avogadro's Law to this statement of fact, we have :—2 molecules of hydrochloric acid gas contain 1 molecule of hydrogen and 1 molecule of chlorine.

Now each molecule of hydrochloric acid gas must contain some hydrogen and some chlorine, so that each molecule of hydrogen and of chlorine must have been able to split up into at least two smaller parts, of which each hydrochloric acid molecule contains one.

In the case of the composition of carbon monoxide and of steam, we decided to call these smaller parts of the oxygen molecule *atoms*. Hence each molecule of hydrogen and of chlorine must contain at least two atoms, or the atomicity of both their molecules = 2.

We have decided to make the molecular weight of hydrogen a standard and have called it 2, so that the atomic weight of hydrogen $= \frac{\text{mol. wt.}}{\text{atomicity}} = \frac{2}{2} = 1$, and the atomic weight of chlorine $= \frac{71}{2} = 35{\cdot}5$.

The formula of hydrochloric acid is thus HCl, and those of the molecules of hydrogen and chorine H_2 and Cl_2 respectively.

We do not know of any other gaseous reaction in which hydrogen takes part which can lead us to the conclusion that its molecule can split into more than two atoms, so that this relationship is generally accepted as correct.

122. The Composition of Salt.—We are now in a position to consider the composition of salt and its relation to hydrochloric acid, which is obtained from it by the action of strong sulphuric acid.

Exp. 125.—(*To be done in the draught chamber.*) Prepare a jar of chlorine, as in Exp. 122, and pour it off into a wide test-tube. Now cut a very thin shaving of metallic sodium (about 4 mm. by 2 mm. in area), put it on a clean deflagrating spoon, and lower it into the test-tube. When the action has finished, carefully dissolve the product in a few drops of water, and evaporate the liquid to dryness in a dish. Test the solid with a flame.

The solid is found to be common salt. We are thus able to make common salt by the direct combination of the two substances sodium and chlorine, so that it is a compound of these two substances only, and is represented by the formula NaCl.

123. The Composition of Water.—We can now apply Avogadro's Law to the volume composition of steam.

We have inferred in Art. 71 that 2 c.c. of hydrogen combine with 1 c.c. of oxygen to form 2 c.c. of steam (above 100°) provided the temperature and pressure are constant. Applying Avogadro's Law, we infer that two molecules of hydrogen combine with one molecule of oxygen to form two molecules of steam.

Now each molecule of steam must contain some oxygen and some hydrogen. As there are two molecules of hydrogen available to form two molecules of steam and only one molecule of oxygen, it appears probable that each molecule of steam contains a molecule of hydrogen, that is, two atoms of hydrogen, combined with half a molecule of oxygen. This can be explained if each molecule of oxygen resembles the hydrogen molecule in being built up of at least two atoms. *An atom* may thus be defined as *the smallest portion of any element which takes part in any chemical change*, and we may define it also as *the smallest portion of any element which takes part in the formation of a molecule.*

124. Molecular Formulae.—The results of investigation of molecular compositions can be represented in a compact form by the use of symbols. Each symbol is used to represent one atom of the element, and we indicate the number of atoms of each element present by means of a number, generally attached as a suffix to the symbol of the element. We can then build up formulae representing molecules, i.e *molecular formulae,* from *symbols* representing atoms.

125. Atomic Weights.—We have already found (Art. 112) that we can compare the molecular weights of any gases, and that if we take the molecular weight of hydrogen as our standard $= 2$, then the molecular weight of oxygen $= 32$; similarly, the molecular weight of chlorine = 71. In the last paragraph, we decided that the evidence we possess shows that the molecules of hydrogen, oxygen, and chlorine each contain two atoms, so that the relative weights of the atoms of hydrogen, oxygen, and chlorine $= \frac{2}{2} : \frac{32}{2} : \frac{71}{2} = 1 : 16 : 35{\cdot}5$.

These numbers are called the *atomic weights*, and may be defined thus :—

The *atomic weight* of an element is the smallest weight of that element which takes part in a chemical change, taking the molecular weight of hydrogen as 2 and its atomic weight as 1.

126. Atomicity.—From the preceding considerations, it may be inferred that the molecule must be built up of a whole number of atoms.

Thus the *molecular weight of an element*

= a whole number × atomic weight.

The whole number is termed the *atomicity* of the element, so that

$$\text{atomicity} = \frac{\text{molecular weight}}{\text{atomic weight}}.$$

In the cases of hydrogen, oxygen, and chlorine the atomicities are, in the ordinary gaseous state, = 2.

127. The Structure of the Atom.—The hypothesis explained above as to the relation of the molecule and the atom has enabled an explanation to be given of the facts of chemical changes. Of recent years, however, a further advance in the study of the atom has been made by the application of electrical methods to chemical phenomena. Very briefly, the modern view considers that the atom of each element is built up of large and heavy particles or *nuclei* surrounded by much smaller particles or *electrons*. Both nuclei and electrons are supposed to be made of the same kind of substance or structure, which is closely related to electricity. The atoms of different elements are built up of different sizes of nuclei with attendant electrons, and the properties of the elements depend on the number of nuclei, the weights of the nuclei, and the number of electrons going to form each atom of that element. Generally speaking, the nucleus and the electrons are differently charged electrically.

Since the nucleus is about 1800 times as heavy as the electron, in the case of hydrogen the lightest element, the weight of one or even several electrons does not affect the atomic weight within the ordinary limits of error in weighing, and for the study of elementary chemistry it will be sufficient to consider that the properties of the atoms, including their atomic weights, are characteristic of the elements we have to study.

128. The Composition of Carbon Dioxide.—We are now in a position to examine the composition of other gases with the assistance of our inductions concerning molecular structure.

Exp. 126.—Take a small piece of charcoal, which will pass through the neck of a bell jar. Select a tightly-fitting cork; fix one end of a piece of copper wire about 20 cm. long firmly into the cork, making it air-tight, and wind the lower end of the wire round the piece of charcoal. Place the bell jar over water, through which you have passed carbon dioxide for five minutes*; fill the jar with oxygen by displacement, and cork it with a spare cork. Now make the charcoal red-hot and keep it in the flame for a minute to make sure that it is quite dry: remove the spare cork, lower the charcoal into the bell jar, and insert the attached cork quickly and tightly. The charcoal burns, the gas becomes hot and expands. When cool, note the volume of the gas, and compare it with the original volume.

We find that the final volume of carbon dioxide is, under the same conditions, equal to the volume of the oxygen from which it is formed, so that we can make an inference about its composition; for since 1 c.c. of carbon dioxide is formed from 1 c.c. of oxygen, by Avogadro's Law one molecule of carbon dioxide contains one molecule of oxygen, *i.e.* two atoms.

In the case of carbon the molecular compositions of many of its compounds have been examined, and it has been found that the quantity of carbon combining with a molecule of oxygen to form carbon dioxide is the smallest portion which takes part in the formation of any molecule containing carbon, and so is assumed to represent one atom, C. Hence we infer that one molecule of carbon dioxide contains one atom of carbon and two atoms of oxygen, and is represented by the molecular formula CO_2.

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* Water may be easily saturated with carbon dioxide by adding a pinch of sodium bicarbonate and a few drops of hydrochloric acid.

129. The Composition of Carbon Monoxide.—The connection between the two oxides of carbon can also be explained. Thus we can carry out an experiment in a similar way to Exp. 82 in a eudiometer, substituting carbon monoxide for hydrogen and finding the volume of carbon dioxide formed by absorbing it in potash solution. It is found that 2 c.c. of carbon monoxide combine with 1 c.c. of oxygen to form 2 c.c. of carbon dioxide. We infer from Avogadro's Law that one molecule of carbon monoxide combines with half a molecule (one atom) of oxygen to form one molecule of carbon dioxide. If the last gas is represented by the formula CO_2, then carbon monoxide is probably represented by the formula CO. The vapour density of the gas is found to be 14 ($H = 1$), so that its molecular weight is 28, which $= 12 + 16$ or one C + one O, thus confirming our formula CO.

130. Gay Lussac's Law of Volumes.—One other point is brought out by the study of the preceding gas reactions. We have noticed that (i) 1 c.c. of carbon dioxide contains 1 c.c. of oxygen ; (ii) 2 c.c. of carbon dioxide contain 2 c.c. of carbon monoxide and 1 c.c. of oxygen ; (iii) 2 c.c. of steam at a temperature above 100° contain 2 c.c. of hydrogen and 1 c.c. of oxygen, and (iv) 2 c.c. of hydrochloric acid gas contain 1 c.c. of hydrogen and 1 c.c. of chlorine.

The fact appears to be that the volumes of gases which enter into chemical change are very simply related ; the volumes are equal or have a ratio to one another involving only small whole numbers such as 1, 2, 3, . . .

This relationship is general and is termed **Gay Lussac's Law of Volumes**, which may be stated thus :—

The volumes of gases which enter into reaction are either equal or related by a small whole number both to one another and to the volume of the product.

Starting as we have done with molecules, we are convinced of the truth of this law, because gases can react only as molecules and form only molecules or atoms in their reactions and not fractions of an atom.

131. Equations.—We have by this time gained the idea that chemical changes are in the main quite definite, so that we are in a position to extend our use of symbols and formulae to represent such changes. An arrangement of formulae which is intended to represent a chemical change is termed a *chemical equation*, or, more shortly, an *equation*. By making our equations represent the molecules of the substances undergoing change both before and after the reaction, we further express what we know about the way in which the changes take place.

It will be simplest first to write out one or two typical equations, and discuss their meaning.

(*a*) *The Decomposition of Mercuric Oxide by Heat.*—To take the decomposition of red oxide of mercury by heat: the equation by which we represent the change is :—

$$2HgO = 2Hg + O_2.$$

(i) This may be read *qualitatively* only, and would run :—

Red oxide of mercury can be decomposed into mercury and oxygen. Nothing is indicated as to the necessity of heating the oxide.

(ii) It may also be read *quantitatively* by assuming that each symbol represents an atomic weight of the element, thus :—

2 (200 + 16) grams of red oxide of mercury can be decomposed into 2 × 200 grams of mercury and 2 × 16 grams of oxygen, *i.e.* 432 grams of red oxide of mercury can be decomposed into 400 grams of mercury and 32 grams of oxygen.

(iii) It can also be read *molecularly*, thus :—

Two molecules of red oxide of mercury can be decomposed into two atoms of mercury and one molecule of oxygen.

This statement requires a little explanation. We have already agreed that the oxygen molecule contains two atoms, but in the case of mercury we find by experiment that its molecular weight is 200; now we agree that its atomic weight is also 200, so that its molecule can contain only one atom, or its atomicity $= \frac{\text{mol. wt.}}{\text{at. wt.}} = \frac{200}{200} = 1$. As we cannot convert mercury oxide into vapour without decomposing it, we do not know its molecular weight, but in this and similar cases we get over the difficulty by a very simple assumption, viz. when in doubt choose the simplest possible satisfactory explanation ; in this case the simplest explanation is that the molecule of red oxide of mercury is built up of one atom of mercury and one atom of oxygen.

(iv) A further extension of the molecular equation can be made, *i.e.* that the volumes of any gaseous substances taking part in a reaction are known. If we use the solution worked out in Art. 115, that the molecular weights in grams of all gases at 0° C. and 760 mm. pressure occupy 22·4 litres.

Hence our equation may finally be read thus :—432 gm. of red oxide of mercury can be decomposed into 400 gm. of mercury, and 22·4 litres of oxygen at 0° C. and 760 mm. pressure.

(*b*) *The Burning of Carbon Monoxide.*—Let us take as another example the explosion of a mixture of carbon monoxide and oxygen, written thus :—

$$2CO + O_2 = 2CO_2.$$

We may read it :—

(i) Carbon monoxide combines with oxygen to form carbon dioxide, but the conditions of ignition are not expressed.

(ii) 56 gm. $\{= 2(12 + 16)\}$ of carbon monoxide combine with 32 gm. of oxygen to form 88 gm. $\{= 2(12 + 32)\}$ of carbon dioxide.

(iii) Two molecules of carbon monoxide combine with one molecule of oxygen to form two molecules of carbon dioxide.

(iv) 44·8 litres of carbon monoxide combine with 22·4 litres of oxygen to form 44·8 litres of carbon dioxide.

(*c*) *Other Oxidations.*—Equations may be written to represent most of the other reactions we have examined; it is better, however, for the present only to write out those which represent the commoner changes, and which do not involve facts we have not to discuss till the later chapters. (It will be good practice to write out, in each case, each of the four points mentioned above.)

In the removal of oxygen from the air by the burning of phosphorus (Exp. 20) the symbol P represents the element. The equation is given thus :—

$$2P_2 + 5O_2 = 2P_2O_5.$$

which may be read :—Phosphorus combines with oxygen to form phosphorus pentoxide.

If the phosphorus is burned in air with the intention of preparing nitrogen (Exp. 32) we must show that there is four times as much nitrogen by volume as oxygen in the air, thus :—

$$2P_2 + 5O_2 + 20N_2 = 2P_2O_5 + 20N_2.$$

In the preparation of carbon dioxide by the burning of carbon in oxygen (Exp. 40) we do not generally indicate that we do not know the molecular weight of carbon, and the usual equation given is :—

$$C + O_2 = CO_2.$$

More properly the equation would be

$$C_n + nO_2 = nCO_2.$$

In the decomposition of carbon dioxide by magnesium (symbol = Mg), Exp. 41, the same difficulty occurs, thus :—

$$2Mg + CO_2 = 2MgO + C,$$

or, more properly,

$$2nMg + nCO_2 = 2nMgO + C_n.$$

The second equation in both cases is, however, very seldom used.

In the case of solutions the symbol Aq is used for water as a solvent. In Exp. 85 we separate alum from sand by solution and filtration : the separation can be expressed in an equation by the use of this symbol, thus :—

$$\text{Alum} + \text{sand} + \text{Aq} = \text{alum, Aq} + \text{sand},$$

the symbol *alum*, *Aq*, showing that a solution of alum is formed, while the sand is left behind.

Having expressed our reactions in equation form, we can use the equations for the purpose of calculation. Thus, for any given change, we can calculate the weight or volume of the products to be obtained from a given weight of the original substances or, vice versa, we can calculate the amount of original substance we must take in order to prepare a given weight or volume of the desired product.

132. The Reactions of Chlorine. Bleaching.—Before passing on we may try to explain certain reactions of chlorine. We have observed the eagerness of chlorine to combine with hydrogen in order to form hydrochloric acid. This gives us a clue to reactions (iv) and (v) of Exp. 122. Thus, when chlorine reacts with turpentine it forms hydrochloric acid and sets free carbon ; we may therefore infer that turpentine is a compound of carbon and hydrogen. When turpentine comes into contact with chlorine, the hydrogen combines with the chlorine, but the carbon does not and so it is set free.

Chlorine also does not bleach colours when dry, but by the addition of water a substance containing hydrogen is introduced : the chlorine combines with the hydrogen, setting oxygen free to combine with the colour and bleach it. An equation can be made thus :—

$$Cl_2 + H_2O + \text{colour} = 2HCl + (\text{colour} + O).$$

In this case the chlorine causes oxidation, and is itself called an *oxidising agent.*

The compounds of chlorine with the elements contain two elements only, and are termed *chlorides*, the termination *-ide* in the name of a compound indicating that it is composed of two elements only. Common salt, the compound of chlorine and sodium, is called *sodium chloride.* Similarly, in the reactions between magnesium and zinc and hydrochloric acid (Exps. 74 and 75), hydrogen is given off and chlorides of the metals are formed. Equations may be written to represent these changes, in which zinc is represented by the symbol Zn, thus :—

$$Mg + 2HCl = MgCl_2 + H_2$$

$$Zn + 2HCl = ZnCl_2 + H_2.$$

133. Acids.—We have used the word *acid* several times, and may now recall what we mean by the name. In the first place, an acid has a sour taste, and turns litmus solution red, and now we may add the further property that its molecules contain hydrogen.

CHAPTER XI.

SALTPETRE: NITRIC AND NITROUS ACIDS.

134. The Examination of Chile Saltpetre.—Among commonly used manures we find two colourless crystalline substances generally called *nitre*, *nitrate*, or *saltpetre*. These substances are obtained from the surface soil in various hot countries. Common saltpetre was imported from India, but another variety called Chile saltpetre is now imported in large quantities from parts of Chile. The surface soil is boiled up with water and the solution allowed to crystallise. The two kinds of saltpetre have many properties in common, and either may be investigated.

Exp. 127.—Take some Chile saltpetre and put one crystal in the flame. Note the effect. Heat some more crystals in a test-tube, and test any gas given off.

We note that Chile saltpetre colours the flame bright yellow, and gives off oxygen when heated. The action of strong sulphuric acid may now be examined.

Exp. 128.—Put a few crystals of Chile saltpetre in a test-tube, and cover them with strong sulphuric acid. Note what takes place. Now warm the tube and note any change.

Though no visible change is noticed in the cold, yet we see on warming that brownish fumes are first given off, and that they are followed by the appearance of a liquid on the sides of the test-tube. This liquid must be investigated.

135. The Preparation and Properties of Nitric Acid.

Exp. 129.—Take a small stoppered retort, and place in it about 25 gm. of Chile saltpetre. Add strong sulphuric acid through

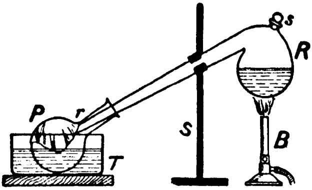

Fig. 71.

a funnel till the salt is covered. Fix the retort in a clamp, slip a flask over its neck, and support the flask in a basin of cold water (Fig. 71). Gently warm the flask until a liquid distils over and collects in the flask. Collect about 10 c.c. Pour a drop into water and test with litmus.

We have thus prepared from saltpetre or nitre a fuming liquid which turns litmus red and is probably an acid. Because it is derived from nitre, it is called *nitric acid*.

Exp. 130.—Place small pieces of metals, *e.g.* magnesium, copper, lead, and zinc, in test-tubes, and pour on each a few drops of nitric acid. Note the reactions.

Pour a few drops of nitric acid on a piece of wood or cloth. Mix two or three drops of the acid with an equal volume of water and warm with some of the white of a boiled egg or a skein of silk ; wash in a few moments. Note the effects.

We observe that nitric acid acts upon metals, and acts more energetically than hydrochloric acid ; it generally dissolves them, and the acid was termed *aqua fortis* on account of this solvent action ; characteristic brown fumes are given off in the process, and these brown fumes are called *nitrous fumes*. Nitric acid also turns vegetable and animal matter yellow.

136. Examination of the Action of Nitric Acid on Metals.

Exp. 131.—(*To be done in the draught chamber.*) Place some copper turnings in a gas jar, pour in a few drops of nitric acid, and cover the jar with a plate. When the reaction stops, remove the cover and pour the fumes into another jar. Now pour a little water into the second jar and shake up. Note the reaction and test the solution with litmus. Repeat the preparation and test the gas in the jar with a burning taper and burning phosphorus.

We note that the nitrous fumes are soluble in water and give an acid solution ; also that they allow brightly burning phosphorus to continue burning.

Exp. 132.—(*To be done in the draught chamber.*) Repeat Exp. 131, using a mixture of equal volumes of nitric acid and water instead of the pure acid. When the gas jar is full, remove the cover and note what you observe.

Repeat the preparation and test the gas with a burning taper and burning phosphorus. Invert a cylinder of the gas over water and pass oxygen into it.

We observe that a mixture of equal volumes of nitric acid and water when poured upon copper gives rise to a colourless or light yellow insoluble gas, which combines with oxygen or air to form nitrous fumes; these dissolve in water, forming an acid liquid. The gas is called *nitric oxide.*

Nitric oxide does not allow a taper or feebly burning phosphorus to burn in it, but brightly burning phosphorus can burn in it.

Exp. 133.—Place some magnesium ribbon in a test-tube and pour on it a mixture of nitric acid with twice its volume of water. Test the gas given off with a lighted taper.

We observe that in this particular case the action of nitric acid with twice its volume of water gives rise to the formation of hydrogen.

137. The Constituents of Nitric Oxide and Nitrous Fumes.—Nitric oxide and nitrous fumes can both be examined by the action of burning phosphorus as in Exp. 20, and it is found that they both yield nitrogen: there is, however, less nitrogen obtained from nitric oxide than from an equal volume of nitrous fumes. Again, both are decomposed by red-hot copper with the formation of copper oxide and nitrogen only. Also nitric oxide forms nitrous fumes by the addition of oxygen.

Both these bodies are, therefore, oxides of nitrogen, and nitrous fumes contain relatively more oxygen than nitric oxide.

138. Formula of Nitric Oxide.—The formula of nitric oxide can be readily found.

***Exp.** 134.—(*Demonstration Exp.*) Take a glass test-tube about 25 cm. long, fill it quickly with dry nitric oxide, and cork it tightly. Now cut a small piece of potassium, open the tube, drop in the metal quickly, and cork again. Warm the tube and melt the potassium, allowing it to run down the tube. When cool, remove the cork under mercury. Measure the length of the tube and the amount of gas left. Test the gas left.

We observe that nitric oxide contains half its volume of nitrogen, that is 2 c.c. of nitric oxide contain 1 c.c. of nitrogen.

Applying Avogadro's Law, we infer that two molecules of nitric oxide contain one molecule of nitrogen. But one molecule of nitrogen contains two atoms. Hence one molecule of nitric oxide contains one atom of nitrogen, and its formula is NO_x.

We find that the vapour density of nitric oxide is 15, so that its molecular weight is 30.

Now if we subtract one atomic weight of nitrogen from the molecular weight, it leaves $30 - 14 = 16$ as the weight of O_x, so that $x = \frac{16}{16} = 1$, and the formula becomes NO.

139. The Preparation of Nitrates.—Nitric acid reacts with caustic soda and caustic potash in a similar manner to hydrochloric acid.

Exp. 135.—Neutralise two portions of nitric acid in evaporating basins with solutions of caustic soda and caustic potash respectively, and evaporate to crystallisation. Compare the solids so obtained with Chile saltpetre and common saltpetre respectively.

Exp. 136.—Evaporate some of the blue solution obtained by the action of copper on nitric acid in Exp. 132. Also dissolve some lead in half and half nitric acid, and filter and dry the crystals formed. Test each of the solids by warming with sulphuric acid and testing the product.

We find that in each case the solid gives off nitric acid, and substances which do this are called *nitrates*.

140. The Action of Heat on Nitrates.

(*a*) *Lead Nitrate.*

Exp. 137.—Heat some dry powdered lead nitrate in a test-tube or small flask fitted with a cork and delivery tube. Collect the gas given off in two cylinders by downward displacement and observe its colour, smell, and density. Test one cylinder by shaking with water and litmus solution. Test the other by burning phosphorus.

We note that the gas is heavy and brown, and has the characteristic smell and properties of nitrous fumes. By a method similar to that set out in Art. 138 we can show that this brown gas has a formula when warm of NO_2; it is called *nitrogen peroxide*.

(*b*) *Saltpetre.*

We have seen that saltpetre gives off oxygen when heated, so we proceed to examine the substance left.

Exp. 138.—Heat about 5 gm. of Chile saltpetre in a weighed hard glass test-tube or crucible, until it stops giving off oxygen. When cool, weigh again and examine the substance left, as to colour, solubility, action of sulphuric acid, etc. Calculate the percentage of oxygen lost on heating.

In an experiment it was found that 2 gm. of the nitrate lost 0·342 gm. of oxygen, or the loss was 17·1 per cent. We note that Chile saltpetre, when heated so as to give off oxygen, leaves a yellowish, fusible and soluble solid which gives off nitrous fumes in the cold when mixed with dilute acids. This yellowish solid contains relatively less oxygen than the original solid nitrate and we can use the above result to determine its composition if we know the formula of the original.

The experimental determination of a formula for nitric acid is difficult. It is, however, represented by HNO_3, Chile saltpetre or sodium nitrate by $NaNO_3$, and saltpetre or potassium nitrate by KNO_3.

We can now fix a formula for the new salt, since it was shown to contain 17·1 per cent. of oxygen less than the original nitrate. Thus if $NaNO_2$ is formed, the loss would be 19 per cent., and if NaNO, 38 per cent. The formula of the new salt is thus probably $NaNO_2$, and it may be considered as a compound of a new acid which is probably represented by the formula HNO_2.

It is usual to give to the salt containing the greater percentage of oxygen a name ending in *-ate*, and to that containing the less percentage a name ending in *-ite*; the names of the corresponding acids end in *-ic* and *-ous* respectively. The last product is thus *sodium nitrite* ($NaNO_2$), and the solution of nitrous fumes in water is *nitrous acid* (HNO_2).

(*c*) *Ammonium Nitrate.*

Ammonium nitrate, which is a very concentrated manure, may next be examined.

Exp. 139.—Take a test-tube, put into it a few crystals (about 1 gm.) of ammonium nitrate, and heat. Note what takes place, and test the gases given off with a burning taper and dried copper sulphate. Go on heating till no more change is seen.

Ammonium nitrate is completely volatilised by heating and appears to give off steam, possibly mixed with some other gas, which we could collect if the steam were removed. The salt also decomposes almost explosively when there is very little of it left.

Exp. 140.—Fit a 250 c.c. flask with a cork and delivery tube for collecting over water : place in the flask about 30 gm. of ammonium nitrate and heat gently. Note the formation of bubbles and observe whether they rise in the usual way. Now put hot water in the pneumatic trough instead of cold and note any difference. Collect several jars of the gas and apply (i) a lighted taper (*a*) at once on removing the lid of the jar and (*b*) after the jar has stood with the lid off for a short time, (ii) a glowing splint, (iii) phosphorus. Stand the last jar over cold water.

We note that when ammonium nitrate is heated a gas is given off which is colourless, heavy, soluble in cold water but insoluble in hot, and which is like oxygen in making burning bodies burn more brightly. The gas is called *nitrous oxide.* When inhaled it produces insensibility, and it is used in the performance of brief surgical and dental operations : during its action it may cause fits of laughter, and so it has been called *laughing gas.*

Nitrous oxide is decomposed by burning phosphorus and by hot metallic copper, and yields only nitrogen and oxygen ; 2 c.c. of the gas are found to contain 2 c.c. of nitrogen, and its molecular weight is 44, so that it is represented by the formula N_2O.

141. The Oxides of Nitrogen.—We can now sum up the formulae and reactions of the oxides of nitrogen.

Nitric acid, which is represented by the formula HNO_3, may be regarded as a compound of water with the oxide N_2O_5 or *nitrogen pentoxide, i.e.* $H_2O + N_2O_5$. This oxide can be prepared, but is apt to be explosive, and readily parts with its oxygen in different stages, yielding in turn *nitrogen peroxide,* NO_2 (or N_2O_4 in the cold), *nitrogen trioxide,* N_2O_3, *nitric oxide,* NO, and *nitrous oxide,* N_2O.

Nitrogen peroxide reacts with water forming *nitric acid*, HNO_3, together with *nitrous acid*, HNO_2, and *nitric oxide*, NO, according to the temperature. Thus with ice-cold water only nitrous acid is formed and with hot water only nitric oxide, while at intermediate temperatures both are present. The difference is due to the decomposition of the nitrous acid by the rise of temperature. Equations may be written to represent these changes :—

$$N_2O_4 + H_2O = HNO_3 + HNO_2 \text{ (Cold)}$$
$$3NO_2 + H_2O = 2HNO_3 + NO \text{ (Hot)}$$
and
$$3HNO_2 = HNO_3 + 2NO + H_2O\cdot$$

These reactions are interesting as showing the ease with which the oxygen compounds of nitrogen can pass into one another. *Nitrogen trioxide* forms with water *nitrous acid*, thus

$$N_2O_3 + H_2O = 2HNO_2.$$

The nitrous acid easily decomposes.

Nitrous fumes are generally a mixture of the peroxide and trioxide of nitrogen with varying quantities of nitric oxide.

142. Tests for Nitric and Nitrous Acids.—Nitrates are among the most important plant foods and are obtained from the soil. They are, however, only present in small quantities, so that we require a test which will readily detect their presence.

Exp. 141.—Make a solution of ferrous sulphate crystals without warming, and put it into two test-tubes. Into (i) pour some saltpetre solution, incline the tube, and pour some strong sulphuric acid down the side (Fig. 72), into (ii) pour some solution of a nitrite, and add dilute sulphuric acid. Note the changes, also the effect of boiling (ii) and gently shaking (i).

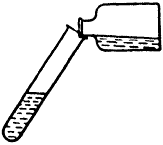

Fig. 72.

We see that a black colour is formed when a nitrite is mixed with dilute sulphuric acid and ferrous sulphate, and also as a *ring* when a nitrate mixed with ferrous sulphate touches concentrated sulphuric acid. In both cases the black solution decomposes on heating, giving off nitric oxide. These reactions are used as *tests for nitrates and nitrites* respectively.

A still more delicate test for nitrates is found in the formation of a green colour with a solution of carbazol in concentrated sulphuric acid.

Exp. 142.—Fill a test-tube about $\frac{1}{3}$ full of well water, add about 2 c.c. of concentrated sulphuric acid, shake carefully, cool, and add a few drops of solution of carbazol in concentrated sulphuric acid. Note the depth of the green colour formed. Repeat the experiment with rain water and other kinds of water, and compare the results.

143. The Air.—We have already examined the air and found that it contains, when pure, nitrogen and oxygen and little else. A question now arises as to whether we can consider it to be a compound of these gases.

In Art. 43 we have defined a compound as a substance with characteristic properties, made up of elements obeying the Law of Constant Proportions.

The composition of the air has been accurately determined by weight to be nearly constant and to be represented by :—

$$\begin{array}{lcr} \text{Nitrogen} & = & 77 \\ \text{Oxygen} & = & \underline{23} \\ & & 100 \end{array}$$

Now in the case of a compound, the molecule must be built up of atoms, so that we must express the ratio of the numbers of atoms of the elements forming the molecule as the ratio of two whole numbers. In the case of air

$$\frac{\text{Number of atoms of nitrogen}}{\text{Number of atoms of oxygen}} = \frac{\frac{77}{14}}{\frac{23}{16}} = 3{\cdot}83.$$

Hence the ratio of the numbers of atoms of nitrogen and oxygen in the possible molecule of air must be represented by 383 : 100, while from its density (Exp. 37) its molecular weight is only 28·8. As these numbers cannot be reconciled, we can only conclude that air is not a compound.

Again, a compound is formed from its elements by chemical change (Art. 70), or decomposed into its elements by chemical change. In the case of air we were able to synthesise it by adding oxygen to nitrogen (Exp. 28), but we did not note any evidence of chemical change, and the simple mixing of the two gases produced ordinary air.

In a chemical change there is also nearly always some marked contrast between the properties of the original constituents and those of the products (Art 70). In the case of air, its characteristic properties are exactly those which we should expect to find in oxygen diluted with nitrogen, and are a sharp contrast to those of the oxides of nitrogen, which are compounds and which we have just examined.

Lastly, we may ask the question, do the properties of the substance, air, agree with those of a compound? This question can be answered in one way by an examination of the solution of air in water.

Exp. 143.—Take a large flask of, say, 2 litres capacity, and fit it with a cork and a delivery tube only just passing through the cork. Boil enough water to fill the flask, and allow it to cool. When cold, shake up the water well with air. Now fill the flask right up to the top, insert the cork, and see that the flask and tube are both quite free from air bubbles. Boil the water in the flask, and collect the gas given off over water in a test-tube. Test it with a glowing splint.

The air which is dissolved in water and expelled by boiling rekindles a glowing splinter and is richer in oxygen than is ordinary air. Hence the oxygen and nitrogen dissolve separately in water, and not as a compound.

We have already made use of a test for free oxygen, viz. that it forms nitrous fumes with nitric oxide. Since nitric oxide forms nitrous fumes in air, the oxygen contained in the air must be free.

Many other arguments can be used which cannot easily be verified by us, and they all agree with the proof we have examined in demonstrating that air is not a chemical compound of nitrogen and oxygen, but that it must be a mixture of these elements.

A *mixture* is a substance made up of two or more different constituents; it may have definite properties, but these properties are not unlike those of its constituents. The constituents are not present in a definite relation to their molecular or atomic weights and they can be separated from one another by methods which do not involve chemical change. Such methods are often called *physical* methods.

CHAPTER XII.

METALS: BASES: SALTS.

144. Metals.—We make use of a large number of substances called metals in everyday life as well as in chemistry, so that we ought to decide how far the term *metal* represents a definite class of bodies with characteristic physical properties and chemical properties.

145. The Physical Properties of Metals.

Exp. 144.—Examine specimens of metals of different kinds, *e.g.* iron, steel, lead, copper, silver, aluminium, magnesium, and tin; also specimens of gold leaf, Dutch metal, etc. Test them for opacity by looking at a candle or gas flame through them (the leaf may be held between two sheets of glass). Examine their behaviour towards heat by holding one end of the piece in a flame by means of the tongs and touching the other end of the metal. Examine their behaviour towards the electric current by seeing if they will ring an electric bell when used instead of one wire. Examine also specimens of sodium, potassium, and calcium, *being very careful not to let them touch anything moist.**

We note that they have a shiny surface, which reflects light in a peculiar way, *i.e.* they are *lustrous*; also they do not allow light to pass through them, *i.e.* they are *opaque*, unless in extremely thin sheets; they become hot at some distance from the part heated in the flame, *i.e.* they *conduct heat*; and they carry the electric current which rings the electric bell, *i.e.* they *conduct electricity.*

---

* The student is specially warned to keep strictly to the instructions regarding the use of sodium and potassium in Exps. 144, 145, 148, and 153. When a piece of sodium heavier than about 0·03 gm. comes in contact with water an explosion may result.

Even gold leaf, which is less than $\frac{1}{250000}$ in. in thickness, preserves its lustre, though it begins to let light pass through.

We also associate other physical properties with the name metal, but these are much more variable than the four preceding properties.

One important property is *hardness*. Steel is one of the hardest substances in common use, though many gems are harder. The property of relative heaviness or high *density* (Art. 11) is also associated with the idea of a metal; lead is very dense, as it is 11 times as heavy as an equal bulk of water; platinum is the densest metal, being 21·5 times as dense as water: on the other hand, aluminium and magnesium are not very dense. Other very useful properties of metals are those of *malleability*, *tenacity*, and *ductility*. A body is said to be *malleable* when it can be hammered or bent into different shapes without cracking. *Tenacity* denotes the property which enables it to resist breaking by stretching forces. *Ductility* denotes the property in virtue of which a substance can be drawn into a fine wire without breaking. Gold is the most malleable and ductile metal; a sovereign could be hammered out to cover 50 square feet or drawn into 10 miles of fine wire.

On the whole, then, we can identify a *metal* as an opaque, lustrous substance, which conducts heat and electricity and possesses to some extent the properties of hardness, comparatively high density, malleability, tenacity, and ductility.

146. The Oxidation of Metals.—We must now examine the chemical properties of the metals, *i.e.* what they do when brought into contact with other elements.

We have already seen that some metals burn to form their oxides when heated in the air or oxygen.

Exp. 145.—Burn a strip of magnesium in air. Heat various metals, *e.g.* copper and iron in a flame, and lead, zinc, sodium, potassium, and calcium on crucible lids. Note the changes and any flame colourations.

We note that many metals change on being heated in the air, and that they give rise to different coloured flames as they burn. We know that oxidation takes place when they burn in air or oxygen, because water is obtained when we pass hydrogen over many of the resulting metallic products at a red heat.

We have also seen that metals are able to decompose steam (Exp. 71), carbon dioxide (Exp. 41), and water (Exp. 72) with the formation of the same oxides, and we may now examine the properties of these oxides. We may also note the characteristic colours produced when different metals burn, and so have a means of identifying them. The most characteristic flame colours noted above are :—

Sodium	bright yellow.
Calcium	orange.
Copper	green.
Potassium	lavender.

147. The Action of Metals on Water.—We have already seen (Exp. 72) that magnesium mixed with mercury is able to decompose water, setting free hydrogen, and also that magnesium decomposes steam ; magnesium also burns in air.

Exp. 146.—Repeat Exp. 72 and filter the milky liquid into an evaporating basin. Burn some magnesium ribbon in air, boil the ash with water in a test-tube, and also filter the liquid into a basin. Taste both liquids and test them with litmus solution. Evaporate both solutions to dryness and examine any residue.

Exp. 147.—Put some small pieces* of calcium into water in an evaporating basin. Note the course of the reaction, and test the gas given off by collecting it in a test-tube filled with water and inverted over the metal. Filter into another basin. Test the solution by tasting, by litmus solution, by passing carbon dioxide gas through it, and by evaporating to dryness. Heat some calcium in air in an iron spoon or patty pan, and when cold drop into water, shake, filter, and test the solution as before. Take some quicklime, add water, shake, filter, and test the solution as before.

Exp. 148.—Take a small piece of sodium, *not larger than a split pea* (see footnote, p. 144), and drop it upon some water in a basin. Note the reaction, and test by litmus and by evaporating the solution to dryness.

* The lumps of calcium obtained commercially can be sawn into slices with a hack saw or reduced by turning or drilling.

We note that the three metals, magnesium, calcium, and sodium, all react with water to give us solutions which turn litmus solution blue, and leave a white residue when evaporated. Such solutions are called *alkaline*, and the dissolved substance is an *alkali*. Thus, starting with three different metals, we end with three substances with similar properties.

Exp. 149.—Dry the solids left on the filter papers in experiments 146 and 147 in basins over boiling water. Heat some of each of the dry solids in dry test-tubes. Note whether any gas is given off, and test by dried copper sulphate.

We note that the solids are similar in giving off water when heated to a red heat, and that they leave white powders which appear to be the same as the oxides with which we started.

Exp. 150.—Take a lump of freshly burned quicklime, weigh it roughly, and pour about one-third of its weight of water upon it. Note any changes, and compare the properties of the quicklime, the water, and the product.

Since quicklime appears to combine with water, which undergoes a permanent change with the giving out of heat, and since both solids obtained from the solutions of magnesium and calcium oxides give off water only when they are made hotter than boiling water, we may assume that definite chemical compounds of water have been formed in both cases. In the case of magnesium the oxide is called *magnesia*, and in the case of calcium the compound of the oxide, quicklime, and water is called *slaked lime*; a general term for a water compound is *hydrate*. In case definite compounds are formed we must investigate carefully any changes of weight.

148. The Hydroxide of Magnesium.

Exp. 151.—Clean, dry, and weigh a porcelain crucible and lid, and into it put about 0·2 gm. of magnesium ribbon cleaned by glass paper; the magnesium should be cut into short lengths and bent zigzag; weigh again. Now heat carefully in a flame until the magnesium begins to burn, remove the flame, and raise the lid carefully to allow air to enter without letting out fumes; repeat the heating, etc., until the metal is all burned and forms a *white ash*. Cool and weigh; repeat the heating and weighing till the weight is constant. Add water drop by drop until the solid remains just moist, and heat over a water bath until quite dry; cool and weigh, and repeat till the weight is constant.

Enter your results thus :—

Weight of crucible + magnesium = 27·068 gm.
,, ,, ,, only = 26·833 gm.
,, ,, magnesium taken = 0·235 gm.
Weight of crucible + magnesium oxide = 27·223 gm.
,, ,, ,, + magnesium = 27·068 gm.
,, ,, oxygen absorbed = 0·155 gm.
Weight of crucible + magnesium oxide + water = 27·397 gm.
,, ,, ,, + magnesium oxide = 27·223 gm.
,, ,, water absorbed = 0·174 gm.

Using these numbers we find that 0·235 gm. of magnesium combines with 0·155 gm. of oxygen to form magnesia, and the latter combines with 0·174 gm. of water to form a hydrate of magnesia.

Since we assume that any compound of oxygen must contain at least one atom in its molecule, *i.e.* at least 16 parts by weight in its molecular weight, we may calculate our results to show this, thus :—

$\frac{.235}{\cdot 155} \times 16$ gm. of magnesium combine with 16 gm. of oxygen and $\frac{\cdot 174}{\cdot 155} \times 16$ gm. of water, *i.e.* 24 gm. of magnesium combine with 16 gm. of oxygen and 18 gm. of water.

149. The Hydroxides of Calcium and Sodium.—Magnesium is practically the only common metal which can be burned in air to form a definite oxide which will combine directly with water to form a definite compound. Several metals, however, decompose water with the formation of a definite compound, which in some cases can be converted into a definite oxide by the expulsion of water by heat, while in other cases it is not so decomposed. An example of the former type is calcium and of the latter sodium.

Exp. 152.—Weigh a clean dry porcelain crucible and lid as in the previous experiment. Place in it about ·5 gm. of freshly sawn calcium and weigh again. Pour into the crucible enough water to cover the calcium, and hold the lid with a pair of tongs over the crucible to prevent loss by splashing. When the reaction is over dry the crucible and slaked lime over a water bath until the weight is constant, and enter the weighings. Now heat the crucible to redness to form quicklime and weigh again, repeating until constant weight is obtained.

Enter your results thus :—

Weight of crucible + calcium = 25·324 gm.
„ „ „ empty = 24·653 gm.
„ „ calcium = ·671 gm.

Weight of crucible + slaked lime = 25·893 gm.
„ „ „ + quicklime = 25·592 gm.
„ „ water = ·301 gm.

Weight of crucible + quicklime = 25·592 gm.
„ „ „ + calcium = 25·324 gm.
„ „ oxygen = ·268 gm.

We find that the ratio of calcium : oxygen : water = ·671 : ·268 : ·301, and calculating for 16 gm. of oxygen, the ratio works out to be

40 : 16 : 18.

Our two experiments thus practically confirm each other as regards whole numbers, and we are dealing with chemical changes which obey the Law of Constant Proportions, in which case we can calculate formulae for the compounds formed, taking O = 16 and H_2O = 18.

Thus, if we take the atomic weight of magnesium as 24 and that of calcium as 40, the formula for magnesia is MgO and for quicklime is CaO, while the formulae for the hydrates are

$MgO + H_2O$ or MgO_2H_2 and $CaO + H_2O$ or CaO_2H_2 respectively. We cannot find the vapour density of any of these substances, but there are other reasons for taking these, the simplest possible formulae, to represent the compounds.

The formula for the hydrate of magnesium may also be written $Mg(OH)_2$, in which case it represents a new class of compound containing oxygen and hydrogen, a *hydroxide.* The corresponding compound of calcium may be written similarly $Ca(OH)_2$, calcium hydroxide or slaked lime. We can now write equations to represent the changes just examined.

$$\left\{\begin{array}{ll} 2Mg + O_2 & = 2MgO \\ MgO + H_2O & = Mg(OH)_2 \end{array}\right.$$

$$\left\{\begin{array}{ll} Ca + 2H_2O & = Ca(OH)_2 + H_2 \\ Ca\,(OH)_2 & = CaO + H_2O. \end{array}\right.$$

Exp. 153.—Heat a very small piece of sodium in an iron spoon : note any change. When cold, dissolve in water and note whether hydrogen is now given off. Test the solution by litmus solution and evaporate some of the solution to dryness. Compare the solid with the solid prepared in Exp. 148. Heat a small quantity of the solid in a test-tube and observe whether water is given off.

It appears from this experiment that sodium combines with oxygen to form an oxide, which dissolves in water, giving a solid with similar properties to those of the hydroxides of magnesium and calcium. We may therefore infer that the sodium compound present is also a hydroxide, *sodium hydroxide* or *caustic soda.*

The experimental proof of the formula of caustic soda is difficult, but if a weighed quantity of sodium is converted into oxide and weighed, and then converted into the hydroxide which is also weighed, it is found that 46 gm. of sodium yield 62 gm. of the oxide and 80 gm. of the hydroxide, a relation which may be symbolised thus :—

$$\begin{array}{lrl} & 4Na + O_2 & = 2Na_2O, \\ & Na_2O + H_2O & = Na_2O_2H_2 \\ \text{or} & & = 2NaOH. \end{array}$$

We are unfortunately unable to determine the vapour density of caustic soda, but for the present we can choose the simplest possible formula to represent it, viz. NaOH. We shall obtain confirmation of this formula later.

150. Neutralisation.

Exp. 154.—Place some caustic soda solution in a basin and add hydrochloric acid until it just turns litmus paper red. Then evaporate to dryness and examine the solid residue : test its reactions with litmus and with strong sulphuric acid.

By the mixing of caustic soda and hydrochloric acid we appear to have produced the same solid, common salt, as was produced by the direct combination of sodium and chlorine only in Exp. 125. The solid does not turn litmus blue, like the caustic soda, nor red, like the hydrochloric acid, nor does it taste like either of them ; it has lost the taste and characters of both alkali and acid, and is said to be *neutral*. The solid contains the metal of the hydroxide, and also the part of the acid which by combination with hydrogen forms the acid, and which is called the *radicle* (or *radical*) of the acid.

Exp. 155.—Repeat Exp. 154 with slaked lime instead of caustic soda, and with nitric acid instead of hydrochloric.

In these cases also substances are formed similar to salt. Such bodies are termed *salts*, so that we may (for the present) define a salt as *the product of the reaction between an acid and a hydroxide of a metal, which contains the metal of the hydroxide combined with the radicle of the acid.*

Since the metallic hydroxides and oxides are much less easily volatilised by heat than the acids they are usually left behind when a salt is heated. They are said to be basic, and a *base* may be provisionally defined as the hydroxide of a metal.

In the formation of salts from acids and hydroxides or oxides water is formed, but no other product, and we can express our results qualitatively in equation form thus :—

$$\mathrm{NaOH + HCl = \underset{\text{sodium chloride.}}{NaCl} + H_2O,}$$

$$\mathrm{NaOH + HNO_3 = \underset{\text{sodium nitrate.}}{NaNO_3} + H_2O}$$

$$\mathrm{Ca(OH)_2 + 2HCl = \underset{\text{calcium chloride.}}{CaCl_2} + 2H_2O.}$$

The salts we have prepared are neutral to litmus solution, and we should now examine the neutralisation more carefully.

Exp. 156.—Take solutions of caustic soda and hydrochloric acid and add litmus to each. Now add the acid to the alkali and note the colour change. Try to find a point where the mixture is neutral, and examine the solution at this point by tasting and evaporation.

Repeat the experiment, adding solutions of cochineal, methyl orange, and phenol-phthalein respectively to both acid and alkali before mixing them.

We observe that we can, from an acid and an alkaline solution, make a neutral solution which on evaporation yields a neutral salt; also that we obtain the point of neutralisation by the use of several different coloured substances, which are called *indicators*.

151. The Composition of Salts.—In agricultural work we buy salts in the form of chemical manures, so that we must find out how far their composition can be assumed to be constant.

Exp. 157.—Weigh out as quickly as possible 50 gm. of pure powdered caustic soda, place it in a half-litre flask or measure, and add distilled water. When it is dissolved and cool, add more water to make the volume exactly one half litre, and shake well. This solution is a 10 per cent. solution. Now by means of a burette (N.B. **it is dangerous to take caustic soda solution into the mouth**) run off 10 c.c. of the solution into one weighed basin and 20 c.c. into another. Neutralise one solution with hydrochloric or nitric acid, using a piece of litmus paper as an indicator, and add excess of hydrochloric or nitric acid to the other; evaporate the two to dryness, then weigh again when cold.

To take an example, using nitric acid:—

Weight of basin + salt from		10 c.c.	20 c.c.
	=	18·50 gm.	28·01 gm.
„ „ „	=	16·38 gm.	23·76 gm.
„ „ salt formed	=	2·12 gm.	4·25 gm.

Now in 10 c.c. of a 10 per cent. solution we have $\frac{10 \times 10}{100}$ gm. of dissolved substance = 1 gm., so that 1 gm. of caustic soda has given 2·12 gm. of common salt, while 2 gm. have given

4·25 gm. of common salt. That is to say, the weights of salt obtained are in the same ratio as the weights of the base taken.

This fact may be stated in the following form :—*Acids combine with bases to form salts in accordance with the Law of Constant Proportions.* It is a very important fact and one of which we make use in comparing and determining the strengths of solutions of acids and alkalies.

152. The Preparation of Nitric Acid Solution and Caustic Soda Solution of known strength.

Exp. 158.—Weigh a dry flask and pour into it *with the greatest care* pure strong nitric acid prepared as in Exp. 129, until the flask weighs 10 gm. more than when empty. Add distilled water, pour the contents into a litre flask ; rinse the small flask, pour the washings into the large one and fill up to the 1000 c.c. mark.

We have now made a solution of 10 gm. of nitric acid in the litre, *i.e.* 1 gm. in 100 c.c., or a one per cent. solution of nitric acid. Measure out from a burette 100 c.c. of the ten per cent. solution of caustic soda prepared in Exp. 157, and dilute it to one litre ; or weigh out 10 grams of the pure powdered caustic soda into a weighed beaker, dissolve in distilled water, transfer to a litre flask with washings from the beaker and make up to 1 litre ; this is a one per cent. solution of caustic soda.

Exp. 159.—Measure out into beakers by a pipette two lots of the acid of 20 c.c. each, and add a few drops of litmus solution to each : the colour must not be more than light red. Rinse out a burette with the one per cent. soda solution, fill it to the zero mark, and fix it in the clamp of the stand. Now run the alkali into the acid in the first beaker, until the colour becomes just neutral. Read the number of c.c. taken, fill the burette again, and repeat the experiment *carefully* with the second beaker : read the number of c.c. taken. Unless these two readings agree exactly, repeat the experiment a third time : if the last two readings very nearly agree, take the average as the true reading. (The first is neglected, as we only do the experiment roughly.) Repeat the experiment, using methyl orange as the indicator, and compare the readings.

Let us take an example :—

20 c.c. of the one per cent. nitric acid required for neutralisa-

tion (i) 13·5 c.c., (ii) 12·7 c.c., (iii) 12·7 c.c. of the one per cent. soda solution. The mean of (ii) and (iii) is 12·7 c.c.

Since both solutions are one per cent., $\frac{12 \cdot 7 \times 1}{100}$ gm. of caustic soda neutralises $\frac{20 \times 1}{100}$ gm. of nitric acid, or 0·127 gm. of caustic soda neutralises 0·20 gm. of acid.

We have decided that 40 gm. represents the formula weight of caustic soda (NaOH), so that the weight of nitric acid required to neutralise 40 gm. of caustic soda $= \frac{40 \times \cdot 20}{\cdot 127} =$ 63 gm.

Now the formula of nitric acid is HNO_3, and its molecular weight $= 1 + 14 + 48 = 63$. Hence we can now represent the neutralisation quantitatively by the equation

$$NaOH + HNO_3 = NaNO_3 + H_2O.$$

This equation is confirmed by the weight of salt obtained from caustic soda in Exp. 157. It was found that 1 gm. of caustic soda gave 2·12 gm. of salt, hence 40 gm. would give 84·8 gm.; this is equal to the weight of salt represented by $NaNO_3$ $(= 23 + 14 + 48)$.

153. The Estimation of Caustic Soda.—We are now in a position to determine the amount of caustic soda in the commercial article.

Exp. 160.—Weigh out a stick of caustic soda as rapidly as possible, dissolve it in distilled water, and make up to one litre. Proceed as in Exp. 159.

Let us assume that the stick of caustic soda weighs 8·94 gm. and that 18 c.c. of the caustic soda solution neutralise 20 c.c. of the one per cent. acid.

Starting with the solution whose strength we are determining, we find that 18 c.c. of unknown caustic soda solution neutralise 20 c.c. of 1 per cent. nitric acid solution,

or 18 c.c. neutralise $\frac{20 \times 1}{100} = 0 \cdot 20$ gm. HNO_3.

But, by the above equation, 63 gm. of the acid neutralise 40 gm. of caustic soda,

$\therefore$ 18 c.c. of the caustic soda solution contain $\frac{\cdot 20 \times 40}{63}$ gm. of NaOH = 0·127 gm. of NaOH.

Also 1000 c.c. (= 1 litre) contain $\frac{\cdot 127 \times 1000}{18}$ gm.

$$= 7{\cdot}06 \text{ gm. of NaOH,}$$

which must have been contained in the original stick weighing 8·94 gm.

Hence the percentage of NaOH in the stick taken is

$$\frac{7{\cdot}06 \times 100}{8{\cdot}94} = 79{\cdot}0.$$

154. The Estimation of Hydrochloric Acid : Preparation of Standard Solution.—Commercial hydrochloric acid (or muriatic acid) has not a constant strength, but a solution of the acid is of great use for analytical work; its strength can be determined on the same lines as that of commercial caustic soda.

Exp. 161.—Measure out about 30 c.c. of concentrated hydrochloric acid in a measuring glass, pour it into a litre flask, make up to the mark and shake well. Measure out 20 c.c. by a pipette, add litmus or methyl orange and run in 1 per cent. caustic soda solution from a burette until neutral.

In one example the volumes of 1 per cent. caustic soda required to neutralise 20 c.c. of the acid were (i) 29·3 c.c., (ii) 29·1 c.c., (iii) 29·1 c.c. The mean of (ii) and (iii) is 29·1 c.c.

That is, 20·0 c.c. of the hydrochloric acid solution neutralise

$$\frac{29{\cdot}1 \times 1}{100} = {\cdot}291 \text{ gm. NaOH.}$$

From the equation of neutralisation,

$$\begin{array}{ccccccc} NaOH & + & HCl & = & NaCl & + & H_2O, \\ 40 & + & 36{\cdot}5 & = & 58{\cdot}5 & + & 18. \end{array}$$

40·0 gm. of caustic soda neutralise 36·5 gm. of hydrochloric acid.

$$\therefore\ 20 \text{ c.c. of the acid solution contain } \frac{\cdot 291 \times 36{\cdot}5}{40} \text{ gm. HCl}$$
$$= \cdot 266 \text{ gm. HCl},$$

$$\text{and } 1000 \text{ c.c. contain } \frac{\cdot 266 \times 1000}{20} = 13{\cdot}30 \text{ gm. HCl.}$$

But 30 c.c. of the commercial acid were diluted to 1000 c.c.

$$\therefore\ 30 \text{ c.c. commercial acid contain } 13{\cdot}30 \text{ gm. HCl},$$

$$\text{and } 100 \text{ c.c. }\quad ,,\quad ,,\quad ,,\quad \frac{13{\cdot}30 \times 100}{30}$$
$$= 44{\cdot}3 \text{ gm. HCl.}$$

It is now easy to prepare a standard 1 per cent. solution of HCl, since 1 litre of the solution already prepared contains 13·30 gm. HCl while the standard should contain 10 gm. only. The method is to calculate the amount of water which is required to dilute 100 c.c. of the strong solution in order to make the standard.

Thus 100 c.c. containing 13·30 gm. of HCl will make $\frac{100 \times 13{\cdot}30}{10}$ c.c. = 133·0 c.c. of a 1 per cent. solution, so that if we add 33 c.c. of water to each 100 c.c. of the solution, the required strength of 1 per cent. will be reached. This can be done either by adding the measured quantity of water or measuring 100 c.c. of the solution in a measuring glass and adding water until the 133·0 c.c. mark is reached.

155. The Formation of Salts.—In addition to the soluble alkaline hydroxides, we find that oxides of most metals are able to neutralise acids and form salts.

Exp. 162.—Take a solution of hydrochloric acid, and shake up portions with (i) magnesia, (ii) litharge (lead oxide, PbO), (iii) iron rust, (iv) copper oxide (CuO). Note the effects, test the liquids with litmus paper. Evaporate the solutions, and examine the solids. Test each with strong sulphuric acid.

We observe that all these insoluble oxides form soluble salts which give off hydrochloric acid when tested by strong sulphuric acid, and are therefore chlorides, and we note colour changes: in the case of litharge the chloride formed is soluble in boiling water, but not in cold. In the formation of these chlorides we may infer that the metallic oxide reacts with the acid to form a salt, while in the previous cases hydroxides entered into reaction.

Exp. 163.—Add caustic soda solution to the solutions of the chlorides (when hot in the case of lead), and note the precipitates. Filter off, wash, and dry them, and compare them with the original oxides. Heat small quantities of the dry solids in test-tubes.

It appears that these chlorides all yield solid precipitates with caustic soda, which, when heated to redness, give off water and leave metallic oxides. These solids must be hydroxides, as in the cases first considered, and it is probable that the chlorides have the same relation to them as in the previous cases.

156. The Electrolysis of Salts.

Exp. 164.—Take an electric battery. Attach to the wires pieces of platinum wire, threaded lengthwise through pieces of platinum foil about 3 cm. × 1 cm. in size (Fig. 73). Place these two terminals or *electrodes* in turn in solutions of (i) copper sulphate, (ii) lead acetate, (iii) iron chloride, (iv) sodium sulphate and litmus; note the results and compare them. (The electrodes may be cleaned after each experiment by dilute nitric acid.)

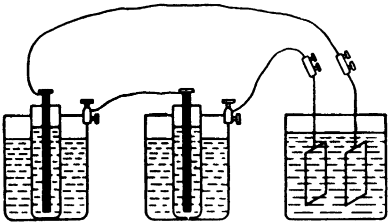

Fig. 73.

It appears that the first three solutions yield a deposit of a metal upon the same electrode, viz. that connected with the zinc of the battery, the *negative* electrode or *kathode*, while oxygen or chlorine appears at the electrode connected with the carbon or copper, the *positive* electrode or *anode.* Now substances which are attracted to the positive plate are themselves negative, and vice versa, so that the metals which appear to be deposited from solution upon the negative electrode are called *electropositive* or *positive elements*. The other elements which are not metallic and are deposited upon the positive electrode are themselves *electronegative* or *negative*. In the last case hydrogen appears at the kathode and no sodium, but the litmus surrounding the kathode is turned blue ; this fact gives us an explanation of what takes place, since it is what we should expect to observe if metallic sodium were deposited in the presence of water : the sodium would react with the water, causing the liberation of hydrogen and the formation of caustic soda.

157. Bases.—We have already seen that the hydroxides and oxides of the metals, even when insoluble in water, are capable of neutralising acids and forming soluble salts, and that these soluble salts yield hydroxides of the metals on the addition of caustic soda. In consequence of this similarity of properties, we group these hydroxides of the metals together under the name of *bases*, and we may now further examine the characteristics of bases.

Exp. 165.—Place on a piece of red litmus paper some potassium hydroxide and some lead hydroxide, prepared as in Exp. 163 and well washed. Note the effect.

We observe that these hydroxides act like those of sodium, calcium, and magnesium in turning litmus blue, so that when soluble, the bases appear to be alkaline.

Exp. 166.—Take a test-tube and put into it a few c.c. of olive oil ; pour into it a little water and shake it up : allow it to stand and note the result. Pour in some caustic soda solution, shake up again, and note the result. Now boil well and allow to cool. Repeat the experiment, using suet instead of oil, and also slaked lime and lead hydroxide respectively instead of caustic soda.

We note that these bases appear to destroy the properties of olive oil or suet and convert it into soap, or an insoluble curdy solid which separates from the water ; this is termed *saponification* of the oil or fat. Hence we may conclude that bases saponify oils and fats. We may include all these points in our definition, thus :—

A *base is a hydroxide of a metal* ; if soluble in water it may turn litmus blue ; it neutralises acids, forming salts, and saponifies fats and oils.

158. The Preparation of Salts.—We have already prepared chlorides by the action of hydrochloric acid solution upon bases and metallic oxides. Before leaving the subject we should examine the action of hydrochloric acid gas upon the bases, basic oxides, and carbonates of some more metals.

Exp. 167.—Fill a dry flask of about one litre capacity with dry hydrochloric acid gas and cork the flask. Place some dry lead hydroxide on a spatula or piece of cardboard: open the flask and quickly pour in the hydroxide. Note what takes place, and repeat with dry lead oxide and other oxides of metals. Test the drops on the sides of the flask by dried copper sulphate.

We confirm our previous observations that the chemical reaction between bases and acids results in the formation of salts and water, and at the same time we note that the oxides of metals also react with the same acid producing the same salts and water. For this reason metallic oxides which act in this way are often included under the term base, though they are more generally called *basic oxides*.

These reactions will be examined again later.

CHAPTER XIII.

SULPHATE OF AMMONIA: AMMONIA.

159. The Examination of Sulphate of Ammonia.—The next substance which we shall examine is a common agricultural product obtained in the manufacture of coal gas, shale oil, etc. In Exp. 1 we noticed that a watery distillate is formed when hay is heated; a similar distillate is formed when coal is heated to form coal gas, and mixes with the water which is used to wash the coal gas, the product being called *gas liquor*. If this gas liquor is neutralised by sulphuric acid, crystals, which are called sulphate of ammonia, separate out on evaporation.

Exp. 168.—Put a few crystals of sulphate of ammonia in a dry test-tube and heat them. Note what takes place.

We note that sulphate of ammonia is converted into a vapour on heating.

Exp. 169.—Put some sulphate of ammonia in a test-tube and add some lime or some solution of caustic soda or potash. Smell the liquid and test the vapour with litmus paper and with moist turmeric paper. Warm it and smell again. Boil it for two or three minutes and smell again.

We observe that sulphate of ammonia is decomposed by caustic alkalies, giving off a vapour with a smell of smelling-salts or *spirit of hartshorn*. The vapour appears to remain in the soda solution until warmed, so that it may be a volatile liquid; we must therefore dry it. Since quicklime is a drying agent and also alkaline when moist, we may try it for the purpose.

160. The Preparation and Properties of Ammonia.

Exp. 170.—Take a flask, and place in it a mixture of slaked lime and sulphate of ammonia. Half fill the flask with lumps of quicklime placed upon the mixture, and warm the flask. The gas again appears to come off. Put a dry gas jar over the neck of the flask (Fig. 74), and when the gas escaping from the lower end of the jar turns litmus paper blue, cover the jar with a dry glass plate : fill four more jars in the same way. (i) Test the first jar with a lighted taper, and find if the gas is heavier or lighter than air, (ii) remove the plate and add a few drops of water, test the liquid by litmus, (iii) invert, remove the plate, and at once put over water in a trough, (iv) put a glass rod dipped in hydrochloric acid in the jar.

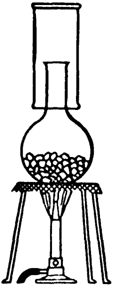
Fig. 74.

The gas which we have prepared appears to have a powerful pungent characteristic smell (of spirit of hartshorn), to put out a lighted taper, to burn for a short time with a greenish-yellow flame, to be lighter than air and very soluble in water. It also forms thick white fumes with hydrochloric acid. It is called *ammonia*.

161. The Composition of Ammonia.—In order to find out the composition of ammonia, we burn it and examine the products.

Exp. 171.—Take a piece of glass tube about 2 cm. in bore and 10 cm. long and fit it with a cork bored with two holes. Through one hole pass a narrow piece of glass tube about 10 cm. long, to which a piece of clay pipe stem is attached by means of an indiarubber tube as in Fig. 75. Through the other hole pass a short bent tube and fill this tube with glass wool. Pass the lower end of the straight tube through a cork fitted into a small flask into which some concentrated ammonia solution or the above mixture is put, and attach the side tube to an oxygen apparatus or cylinder. Gently warm the flask and pass oxygen slowly into the apparatus, at the same time applying a lighted taper to the pipe stem.

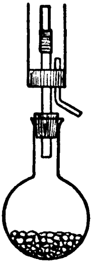
Fig. 75.

The ammonia burns with a bright greenish-yellow flame, and it forms a mixture of steam and nitrogen, so that it must contain nitrogen and hydrogen, and it may contain oxygen. The gas is decomposed when electric sparks are passed through it, and only nitrogen and hydrogen are formed, so that it does not contain any oxygen. Further, chlorine decomposes ammonia gas, forming hydrochloric acid and nitrogen only, with no trace of oxygen or water, so that, taking all these experiments together, we may assume that ammonia is a compound of nitrogen and hydrogen only. It may be considered as a *hydride* of nitrogen (see Art. 132).

The decomposition of ammonia by chlorine also enables us to find a formula for ammonia.

Exp. 172.—Fill a test-tube of chlorine prepared as in Exp. 123, and close the mouth with the thumb. Place some strong solution of ammonia in a basin, invert the test-tube in the solution, and remove the thumb. Note the height to which the liquid rises. Remove the test-tube, closing it with the thumb, and stand it over water, and then over dilute hydrochloric acid. Note the final volume of the gas and test it.

We find that the tube full of chlorine is replaced by about one-third of the tube full of nitrogen, that is we obtain 1 c.c. of nitrogen from the ammonia which is decomposed by 3 c.c. of chlorine.

But each c.c. of chlorine, in forming hydrochloric acid, combines with an equal volume of hydrogen, and all the chlorine is found to be used up by the ammonia, with the formation of hydrochloric acid.

Hence in ammonia each 1 c.c. of nitrogen must be combined with 3 c.c. of hydrogen, or applying Avogadro's Law, each molecule of nitrogen must have been combined with three molecules of hydrogen.

Exp. 173.—Find the weight of a flask of dry ammonia as in Exp. 76, and calculate the vapour density.

We find that the vapour density is about 8·5, so that the molecular weight of ammonia is about 17.

Now we have found that the molecular weight of nitrogen is 28 and that of hydrogen is 2, so that 1 molecular weight of nitrogen and 3 molecular weights of hydrogen should weigh $28 + 6 = 34$, that is 17×2.

Hence a molecular weight of ammonia (= 17) can only be made up of 1 half molecular weight of nitrogen and 3 half molecular weights, *i.e.* 3 atomic weights of hydrogen.

Thus the molecule of ammonia is represented by the formula NH_3. The atomicity of nitrogen is 2, and each molecule of nitrogen must be able to split up into at least two smaller parts or atoms, and the atomic weight of nitrogen $= \frac{28}{2} = 14$.

The above argument can be written out in another way.

If we assume that 1 molecule of nitrogen contains 2 atoms, and 3 molecules of hydrogen contain 6 atoms, the molecular formula of ammonia is expressed by $(N_2H_6)_x$.

Now the molecular weight = 2 × vapour density, so that the molecular weight $= 2 \times 8{\cdot}5 = 17$.

Hence $$(N_2H_6)_x = 17,$$

or $$x = \frac{17}{2N + 6H} = \frac{17}{(2 \times 14) + 6} = \frac{17}{34} = \frac{1}{2},$$

and $$\tfrac{1}{2}(N_2H_6) = NH_3,$$

which is the formula for ammonia.

162. Sal Ammoniac.—We have seen (Exp. 170) that hydrochloric acid and ammonia form dense white fumes when brought together.

Exp. 174.—Take gas jars of hydrochloric acid and ammonia gases, place them mouth to mouth (Fig. 76), and pull out the glass covers. Note the reaction and examine the product.

The fumes are found to condense to a white solid. Water does not appear to be required for the formation of the solid, and the substance must be formed by direct combination of the acid and ammonia. It is called *sal ammoniac*. A more careful examination of the volume combination gives us a clue to the formula of sal ammoniac.

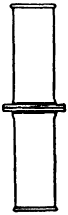

Fig. 76.

***Exp. 175.**—(*Demonstration Exp.*) Put some paraffin oil, which has been standing with quicklime in order to dry it, in a pneumatic trough. Fill a dry test-tube with dry hydrochloric acid over the oil, and decant the gas up into a boiling tube. Wash and dry the test-tube, fill it with dry ammonia, and decant up into the hydrochloric acid. Note the result.

We observe that sal ammoniac is formed, and that no gas is left over, so that the ammonia and hydrochloric acid have combined in equal volumes to form sal ammoniac. A simple equation can now be made to represent the reaction, thus:—

$$NH_3 + HCl = NH_4Cl,$$

and in absence of any reason to the contrary we can assume that the formula of sal ammoniac is NH_4Cl.

163. The Estimation of Ammonia.—The preceding determination of a formula for sal ammoniac is hardly accurate enough for use in the estimation of ammonia.

> **Exp. 176.**—Dry an evaporating basin over a water bath and weigh it when cold. Put into it 50 c.c. of your 1 per cent. solution of hydrochloric acid, and add a solution of ammonia until the mixture turns litmus paper blue. Evaporate to dryness over the water bath, cool, and weigh again. Test the solid with litmus paper and a drop of water.

The difference between the weighings is the weight of sal ammoniac formed from the acid in the 50 c.c. taken, *i.e.* from 0·5 gm. of hydrochloric acid.

Thus if the sal ammoniac weighs 0·73 gm. and the hydrochloric acid 0·5 gm., the ammonia must weigh 0·23 gm. Calculating the weight of ammonia required to combine with a molecular weight, *i.e.* 36·5 gm. of the acid, we find that it is 17 gm., which is a molecular weight of ammonia.

This confirms the equation given in the preceding paragraph as representing the reaction between ammonia and hydrochloric acid which results in the formation of the neutral sal ammoniac, and we can use it to enable us to estimate the quantity of ammonia contained in a solution.

> **Exp. 177.**—Pour some strong ammonia solution into a burette and measure out 10 c.c. into a litre flask. Make up to the mark with distilled water and shake well. Measure out lots of 20 c.c. by a pipette and neutralise with 1 per cent. hydrochloric acid solution, using methyl orange or litmus as an indicator.

We may assume as an example that the average number of c.c. of the acid solution required for neutralisation = 12·6. Thus 12·6 c.c. 1% HCl neutralise 20 c.c. ammonia solution.

Now 100 c.c. 1% HCl contain 1 gm. HCl.

$$\therefore\ 12{\cdot}6 \text{ c.c. } 1\% \text{ HCl contain } \frac{12{\cdot}6 \times 1}{100} = {\cdot}126 \text{ gm. HCl.}$$

From the equation

$$HCl + NH_3 = NH_4Cl,$$

36·5 gm. HCl neutralise 17 gm. NH_3.

$$\therefore \cdot 126 \text{ gm. HCl neutralise } \frac{\cdot 126 \times 17}{36\cdot 5} = \cdot 0587 \text{ gm. } NH_3,$$

which must be contained in 20 c.c. of the diluted solution used.

Hence 1000 c.c. of the diluted solution or 10 c.c. of the original solution contain $\frac{\cdot 0587 \times 1000}{20} = 2\cdot 94$ gm. NH_3,

and the original solution contains $\frac{2\cdot 94 \times 100}{10} = 29\cdot 4\%$ NH_3.

If desired, this solution can be diluted to 1%, as in Exp. 161.

164. Tests for Ammonia.—Ammonia is of great agricultural importance, and the common test of boiling with soda and testing the steam given off by litmus or turmeric paper might allow us to overlook very small traces in any solution.

Exp. 178.—Pour a couple of drops of ammonia solution into a test-tube, fill with water and empty, and then fill half full of water. Add to this water a few c.c. of caustic soda solution and about 2 c.c. of Nessler's solution. Note the colour and compare with that produced by using rain water, distilled water, and surface well or river water.

We observe that very dilute ammonia solutions give a colour with Nessler's solution which varies from pale yellow to deep golden brown, according to concentration, and that different specimens of water appear to contain varying quantities of ammonia.

165. Relation between Nitrates and Ammonia.

Exp. 179.—Place a few crystals of sodium nitrate in a test-tube, add some iron filings or aluminium foil, and caustic soda solution, and boil. Test the steam with red litmus or turmeric paper.

We note that ammonia is given off, so that the nitrogen oxide in the nitrate appears to be converted into nitrogen hydride by the action of metals in caustic soda solution; this is a process of reduction.

166. The Cycle of Nitrogen in Plant and Animal Life.—We have already examined the cycle of carbon in plant and animal life (Art. 45). The cycle of nitrogen is even more interesting and important, but it is more complicated and more difficult to study completely; we can, however, investigate a simple case.

Exp. 180.—Heat some gelatin, albumen, hair, or other animal product with slaked lime (or better, soda lime) in a dry test-tube and test the fumes with moist litmus and turmeric papers, as in Exp. 169. Test the same substances for ammonia by boiling with caustic soda solution, and for nitrates by ferrous sulphate and strong sulphuric acid, as in Exp. 141.

We note that animal tissues contain nitrogen, since they yield ammonia when heated with soda lime, but that it is not present as ammonia or nitrates. Since the substances char and give off water it is probable that the nitrogen is in combination with carbon and other elements in the organic matter.

Exp. 181.—Pound up some vegetable matter, *e.g.* a turnip, wheat, or beans, with a small quantity of water, and test the extract and the residue as above.

We note that the plant juice contains nitrates and ammonia, and that the solid tissues contain combined nitrogen, which is also probably organic.

Exp. 182.—Collect some of the surface soil of a garden plot in the summer, warm with water, and test both soil and extract as before.

We note the presence of nitrates in the extract, and combined organic nitrogen in the soil.

Exp. 183.—Moisten some of the surface soil obtained for the last experiment with a very dilute solution of sulphate of ammonia. Keep the moist soil warm for a few hours, and extract a portion of it from time to time with distilled water as in the last experiment. Test the extract for ammonia and for nitrates.

We note that the ammonia gradually disappears, and that the nitrates increase in quantity.

These facts are most easily explained by an examination of the food and the waste products of plant and animal life, and confirmed by observations on manuring.

The ordinary green plant obtains its nitrogenous food from the soil water in the form of nitrates, and builds them up into organic compounds of nitrogen in its tissues. These organic nitrogen compounds may either be consumed by animals and appear in their waste products as compounds related to ammonia and return to the soil in manure, or they may return to the soil direct and undergo a similar change under the action of bacteria living in the soil. The ammonia derivatives are then changed by other kinds of bacteria into nitrites and then into nitrates in the soil. This *nitrification*, as it is called, is evidently a process of oxidation, and requires a warm temperature to bring it about. The nitrates are then ready to begin the cycle again as plant food.

CHAPTER XIV.

SULPHUR.

167. The Examination of Sulphur.—We meet the substance sulphur commonly in the two forms of brittle rolls, *roll sulphur*, and of a fine powder, *flowers* or *flour of sulphur*. Both of these have a characteristic yellow colour.

Exp. 184.—Examine specimens of sulphur. Shake and boil some sulphur with water, filter and evaporate the filtrate to dryness : note if any residue is left. Heat a small quantity of sulphur on a crucible lid : note any changes.

We observe that sulphur is insoluble in water, and that when heated it melts, turns brown, and then burns with a blue flame. The colour change is worth more careful examination.

Exp. 185.—Take a boiling tube or small round-bottomed flask, and in it place about 50 gm. of sulphur. Warm it gently over a small flame, shaking it all the time. Note any changes and allow it to cool.

We see that sulphur, when heated, first melts to a yellow liquid which rapidly darkens in colour ; it then becomes very viscous and brown ; finally it becomes more liquid again, remaining dark brown until it boils, when the vapour condenses as a yellow powder in the upper part of the tube or neck of the flask. As it cools it gradually loses its dark colour, and appears to crystallise, and in course of time it becomes yellow again.

Exp. 186.—Take a small beaker or fireclay crucible, and in it put about 30 gm. of sulphur. Heat it gently over a small flame till the sulphur is just melted, and then remove the flame. When

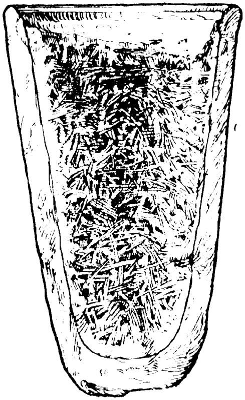

Fig. 77.

crystals are seen to be forming, break the crust with a rod and pour off the liquid, leaving the crystals in the beaker or crucible (Fig. 77): note their shape.

Exp. 187.—Reheat the sulphur used in Exp. 185, and when it has become viscous and just thin again, pour the liquid into water. Note the characters of the solid and compare it with that obtained in the preceding experiment.

We note that sulphur can be prepared in three different forms by the action of heat, viz. a powder, an elastic (plastic) solid, and long prismatic crystals (Fig. 77), called respectively *flowers of sulphur*, *plastic sulphur*, and *prismatic sulphur*. Since these are actually made from sulphur and sulphur only, they can only be forms of the same substance.

Now although sulphur does not dissolve in water, yet it is soluble in some other liquids.

***Exp. 188.**—(*Demonstration Exp.*) Take a boiling tube and loosely fitting cork. Into the tube put some pieces of sulphur and upon them pour some carbon disulphide (say 10 c.c.). Shake up. Note the colour of the liquid. Now pour the liquid into a large watch glass or basin, and place it in the open air to evaporate slowly. Note the shape of the crystals formed.

N.B.—The student is cautioned that carbon disulphide is a very volatile and extremely inflammable liquid, and that it is therefore **very dangerous** to bring carbon disulphide within a yard of a flame.

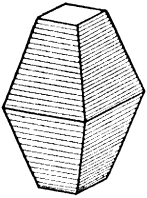

Fig. 78.

Sulphur dissolves in carbon disulphide, and crystallises out from the solution in crystals of the type called *octahedral* (Fig. 78). Sulphur, therefore, has two different crystalline forms as well as two different forms (flowers and plastic) which are not crystalline; these non-crystalline forms are called *amorphous*. Sulphur is an element and is represented by the symbol, S.

168. Allotropy.—When a single element, as in the case of sulphur, exists in various forms which have different physical properties, these forms are called *allotropic forms* of the element. Thus sulphur exists in four different allotropic forms. Another element which has several allotropic forms is carbon. This exists in the forms (*a*) charcoal and lamp black, which are amorphous, (*b*) blacklead or graphite, which is crystalline, and (*c*) diamond, which is crystalline, colourless, and transparent, and which is also the hardest substance known. These can be proved to be allotropic forms of carbon by burning them to carbon dioxide.

169. The Oxidation of Sulphur.—Sulphur burns in air and in oxygen, and the reaction should be examined.

Exp. 189.—Take a gas jar, fill it with oxygen, and burn in it a piece of roll sulphur on a deflagrating spoon. Note the reaction. Test the gas with a burning taper, paper dipped in a solution of potassium dichromate, iodic acid and starch, water, and litmus solution.

We note that sulphur burns in oxygen to form an oxide, which has a characteristic smell, puts out a burning taper, is soluble in water, turns potassium dichromate paper green, turns iodic acid and starch blue, and turns litmus red, *i.e.* it forms an acid solution. This gas also appears as a product of many other reactions, and is called *sulphur dioxide.*

Exp. 190.—Heat in a test-tube a small quantity of powdered iron pyrites. Heat also (i) iron, (ii) copper, (iii) charcoal, in test-tubes with a few drops of sulphuric acid. Note any changes and any gaseous products.

In roasting iron pyrites and in heating elements with sulphuric acid, we note the formation of the same gas as is formed when sulphur burns in oxygen. Hence we infer that both pyrites and sulphuric acid contain sulphur, and that we shall probably be able to prepare sulphur dioxide by one of the above reactions.

170. The Preparation and Properties of Sulphur Dioxide.

Exp. 191.—Fit a small (200 c.c.) flask with a cork, thistle funnel, and delivery tube bent at right angles, and connected by a short indiarubber tube with a straight glass tube. In the flask place some copper turnings, and cover them with some strong sulphuric acid. Warm the flask and note the change and the evolution of gas. As we have seen that the gas is soluble in water, we must collect it by displacement. Find if it is heavier or lighter than air, and collect four or five jars of the gas. Test it as in Exp. 189, also with permanganate of potash solution. In a jar of the gas place some blue flowers or rose petals.

We observe that the gas is much heavier than air, turns permanganate of potash colourless, and bleaches flowers.

Exp. 192.—Place the bleached flowers or rose leaves in dilute sulphuric acid and warm. Note any changes of colour.

The bleaching by sulphur dioxide differs from that by chlorine because the bleached colour can be more or less restored; the change will be reconsidered later.

171. The Molecular Formula of Sulphur Dioxide.

If we repeat Exp. 126, burning sulphur instead of carbon in oxygen, we find that sulphur dioxide contains its own volume of oxygen, that is each molecule of the gas contains one molecule or two atoms of oxygen. Further, we find that sulphur combines with its own weight of oxygen to form sulphur dioxide, and 32 gm. of sulphur combine with 32 gm. (= molecular weight) of oxygen to form 64 gm. of the oxide. Also we find that the vapour density of the gas is about 32, so that its molecular weight is 64.

Now we never find less than 32 parts of sulphur in any molecular weight, so that 32 is taken as the atomic weight of sulphur, and the formula of the gas is SO_2.

172. The Properties of Sulphur Dioxide Solution.

Exp. 193.—Make a solution of sulphur dioxide by passing the gas prepared as in Exp. 191 through water. Measure out 20 c.c. of the solution, add litmus, and run in caustic soda solution (about 10 per cent.) till it is neutral: evaporate and crystallise out the solid formed. Examine the crystals with a lens and test the solid by strong sulphuric acid.

We note that sulphur dioxide solution is acid to litmus, and makes a neutral solid salt with caustic soda. The solution is called *sulphurous acid*, and the salt is called a *sulphite*.

The acid has probably the formula H_2SO_3 ($= H_2O + SO_2$) and the sulphite the formula Na_2SO_3.

173. The Oxidation of Sulphur Dioxide. Sulphuric Acid.—Sulphur dioxide solution allowed to stand in air or oxygen gradually loses its smell and absorbs oxygen, but it remains acid, and on evaporation leaves a small quantity of a heavy, oily liquid. This is probably an oxidation product, so the oxidation of sulphur dioxide must be studied.

***Exp. 194.**—(*Demonstration Exp.*) In a piece of hard glass tubing place some spongy platinum or platinised asbestos (prepared by soaking asbestos in a solution of platinum chloride and ammonium chloride and afterwards making it red-hot). Make a strong solution of sulphurous acid and place it in a wash bottle. Attach to the entry tube of the wash bottle a test-tube containing potassium chlorate and manganese dioxide, and to the exit-tube the tube containing the platinised asbestos. Support this tube horizontally and attach to the other end of it a tube bent down as shown in Fig. 79. Heat the test-tube slowly and gently warm the horizontal tube. Note the appearance of fumes: collect them in a dry flask. Remove the test-tube, and add water to the flask containing the fumes. Test the solution with litmus and smell it. Boil the solution and test it again, and also test it with potassium dichromate, potassium permanganate, and iodic acid and starch.

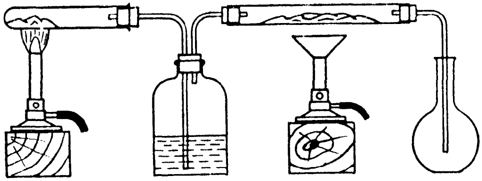

Fig. 79.

We note that white fumes are formed, which are soluble in water and give an acid solution not decomposed by boiling. This solution is different from sulphurous acid, and since it does not remove oxygen from the oxidising agents it probably contains more oxygen than that acid.

The complete proof of the composition of the new oxide of sulphur and of the acid formed when it dissolves in water is difficult to demonstrate experimentally, but we may represent the new oxide, which is called *sulphur trioxide*, by the formula SO_3, while the acid formed when the oxide dissolves in water is represented by H_2SO_4, and is called *sulphuric acid*, thus :—

$$2SO_2 + O_2 + \text{spongy platinum} = 2SO_3 + \text{spongy platinum},$$

$$SO_3 + H_2O = H_2SO_4.$$

Note.—The student should examine a specimen of solid sulphur trioxide, and also examine its reaction with water.

We can demonstrate the identity of our new acid and sulphuric acid by a test.

Exp. 195.—To solutions of sulphurous and sulphuric acids and our own acid solution add hydrochloric acid and a solution of barium chloride ; compare the results.

The formation of a white precipitate with barium chloride and hydrochloric acid is a *test* for the presence of sulphuric acid.

We can now explain more fully the reaction observed above, in which sulphurous acid is converted into sulphuric acid by the absorption of oxygen.

We confirm our inference that the sulphurous acid was changed by oxidation, and note that it has been oxidised to sulphuric acid. An equation may be written to represent this reaction thus :—

$$H_2SO_3 + O \text{ (from an oxidising agent)} = H_2SO_4.$$

Similarly, the bleaching action of sulphurous acid noted in Exp. 191 is explained by the reducing action of the sulphurous acid.

174. The Manufacture of Sulphuric Acid.—The conversion of sulphur dioxide into sulphuric acid by direct combination with oxygen and water under the influence of spongy platinum is used for the preparation of sulphuric acid. Other methods of oxidation can be used, but by far the most important method from an agricultural point of view is the use of nitrous fumes.

Exp. 196.—Place some copper turnings in a gas jar, pour on a few drops of nitric acid, and cover the jar. When the action stops, pour the fumes into a dry jar, and pour in a few drops of sulphurous acid. Note any changes and try the effect of lifting the lid and of adding water. Test for sulphuric acid as in the last experiment.

We note that nitrous fumes can oxidise sulphurous to sulphuric acid, and that nitric oxide is formed; this gas, as we have already found, combines with the oxygen of the air again to re-form nitrous fumes: this reaction is the basis of the method adopted for the manufacture of sulphuric acid.

If we adopt the formula NO_2 to represent nitrous fumes, then the reactions can be represented by the equations :—

$$NO_2 + SO_2 + H_2O = H_2SO_4 + NO,$$

$$2NO + O_2 = 2NO_2.$$

Gases generally occupy a large volume relatively to their weight, so that the apparatus required to make a ton of sulphuric acid in a short time must be large; also since air is used to supply the oxygen, the capacity of the apparatus must be still greater in order to hold the nitrogen too.

The reactions are conducted in large chambers made of sheet lead, on which metal dilute sulphuric acid and the gases used have little action. Into one end of the chambers are led the sulphur dioxide, nitrous fumes, air, and steam, and from the other end is carried away the waste nitrogen. Since the nitrous fumes are regenerated it should not be necessary to add any more when once the chamber is charged with them, but a small amount of the oxides of nitrogen is always being carried away in the waste nitrogen and must be replaced.

The sulphur dioxide is made by burning sulphur upon a shallow tray when the acid is required pure, or by burning iron pyrites, FeS_2, or copper pyrites, $(CuFe)S_2$, in a deep grate when a less pure acid will do, the furnaces in which the burning is effected being called the *kilns* or *burners* (Fig. 80). After allowing the dust given off from the burners to settle in a flue, the mixture of sulphur dioxide and nitrogen is charged with enough nitrous fumes to replace the waste, either by the action of sulphuric acid on sodium nitrate contained in cast-

PLANT FOR MANUFACTURE OF SULPHURIC ACID. SCALE 18 FT. TO THE INCH.

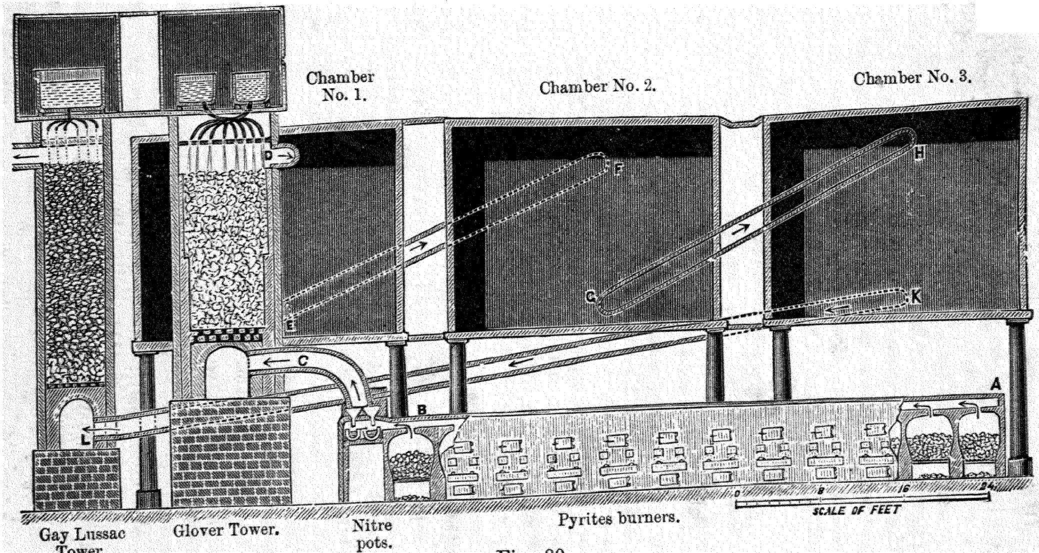

Fig. 80.

iron pots (*nitre-pots*) placed in the flue carrying the sulphur dioxide to the chamber, or else by the addition of the necessary quantity of nitric acid to the acid entering the top of the Glover tower, Fig. 80 (see later).

When the gases leave the furnace flue they are too hot to react; they are mixed with the quantity of air required to complete their oxidation and passed up a first tower down which trickles some of the dilute sulphuric acid prepared in the chamber; this stream of acid becomes more concentrated by loss of water which makes the furnace gases cooler and moister. When the gases reach the chamber they receive a fine spray of wet steam, and the reaction which takes place causes a deposit of dilute sulphuric acid in the form of a fine rain of acid, *chamber acid.*

The nitrous fumes which are carried away in the stream of nitrogen are regained by making the waste gases pass up a high tower lined with tiles and filled with hard coke or tiles, down which is trickled a stream of the concentrated acid which is prepared in the first or Glover tower; this concentrated acid is able to absorb the nitrous fumes, so that practically pure nitrogen passes on to the chimney. This second tower is called the *Gay-Lussac* tower.

Now it has been found that when the concentrated acid containing dissolved oxides of nitrogen (*nitrated acid*) is diluted, it gives off the dissolved gases, so that they can be restored to the chamber if they can be set free in the first tower. Hence the nitrated acid is pumped to the top of the first tower and allowed to trickle down into the tower together with the dilute acid from the chamber; the dilution sets free the nitrous fumes, which are restored to the chamber, and then the dilute acid is again concentrated by the ascending stream of hot burner gases, as we have already noted. The tower in which this reaction takes place, the first tower, is shorter and wider than the Gay-Lussac tower, it is lined with fire-brick and filled with flints, and it is called the *Glover* tower.

If the acid is required more concentrated than that falling through the Glover tower, it is concentrated in glass or platinum stills.

The chamber process is continuous and is worked on a large scale for the manufacture of superphosphates and sulphate of ammonia.

175. The Properties of Sulphuric Acid. Basicity.—When a solution of sulphuric acid is evaporated and then further concentrated by boiling it leaves an oily liquid, strong or concentrated sulphuric acid, some of whose properties we already know (Exp. 190).

Exp. 197.—Pour a few drops of sulphuric acid on some cloth and note the effect. Carefully pour some sulphuric acid on a lump of sugar, into some syrup of sugar, on paper, and into water.

Sulphuric acid is a heavy oily liquid with a high boiling point, it chars organic matter, but dissolves paper, and when heated with many of the elements yields sulphur dioxide (Exp. 190). When diluted it gives out heat and the dilute acid acts upon zinc, giving off hydrogen (Exp. 75).

The action of sulphuric acid on copper can be represented by an equation, thus :—

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2.$$

Exp. 198.—Weigh a beaker, and pour into it 100 gm. of pure concentrated sulphuric acid. Pour the acid carefully into a litre flask about half full of distilled water, shaking the liquid as you pour the acid in. Rinse the beaker with distilled water, and pour the rinsings into the flask ; finally make up the solution to a litre by distilled water. This makes a 10 per cent. solution of sulphuric acid.

Now measure out two lots of 20 c.c. of the acid into basins ; neutralise one by 10 per cent. caustic soda solution added from a burette, and to the other add half the volume of the caustic soda solution required to neutralise it. Evaporate both solutions to dryness and examine the solid residues ; test them with litmus, by heating alone, and by heating with saltpetre.

We observe that sulphuric acid forms two different salts with caustic soda, one of which is neutral and the other acid. These salts are called *sulphates*.

Further, we find that 20 c.c. of the 10 per cent. acid require for neutralisation 16·3 c.c. of the 10 per cent. caustic soda solution to form the neutral salt, that is 1·63 gm. of caustic soda neutralise 2·0 gm. of sulphuric acid. But the formula of caustic soda, NaOH, represents $(23 + 16 + 1) = 40$ gm., and 40 gm. of caustic soda neutralise, from our experiment,

$$\frac{40 \times 2\cdot0}{1\cdot63} \text{ gm. of sulphuric acid} = 49 \text{ gm. of sulphuric acid.}$$

But since the formula of sulphuric acid, H_2SO_4, represents $(2 + 32 + 64) = 98$ gm., then 98 gm. of sulphuric acid must be neutralised by $\frac{98 \times 40}{49} = 80$ gm. of caustic soda; this is twice the amount represented by NaOH, or is equal to that represented by 2NaOH. The equation representing neutralisation must therefore be :—

$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O$$

and the neutral salt is *normal sodium sulphate*, represented by the formula Na_2SO_4.

The formation of the other, the acid salt, with half the quantity of caustic soda must be represented by the equation :—

$$NaOH + H_2SO_4 = NaHSO_4 + H_2O$$

and the salt itself, the *acid* or *hydrogen sodium sulphate*, by the formula $NaHSO_4$.

In a similar manner sulphurous acid forms two sulphites, a normal sodium sulphite represented by Na_2SO_3 and an acid sodium sulphite represented by $NaHSO_3$.

Acids such as sulphuric and sulphurous acids, whose molecule contains two hydrogen atoms replaceable separately by metals and which form two different kinds of salts, are called *dibasic* acids, while those like hydrochloric and nitric acids, which contain only one hydrogen atom replaceable by metals and form only one kind of salt, are called *monobasic* acids, and the property of acids which fixes the number of replaceable atoms of hydrogen and also the number of different salts which can be prepared from any acid, is called their *basicity*.

The salt in which both hydrogen atoms are replaced is called the *normal* salt, while that in which only one is replaced is called the *acid* or *hydrogen salt*; a normal salt is not necessarily neutral.

176. The Estimation of Sulphuric Acid.—The formation of a neutral solution when both the hydrogen atoms in the acid molecules are replaced by sodium enables us to ascertain the weight of sulphuric acid contained in a solution or the percentage of the acid sulphate contained in a sample of that salt.

Exp. 199.—Dilute 10 c.c. of commercial oil of vitriol, such as is used in the manufacture of superphosphate, to 1 litre, taking care to shake as the dilution proceeds. Pipette out 20 c.c. of the diluted acid, which is a 1 per cent. solution, add litmus or methyl orange, and run in 1 per cent. caustic soda until neutral.

In one experiment the average number of c.c. of caustic soda solution required was 10·4.

That is, 20 c.c. unknown acid solution were neutralised by 10·4 c.c. 1 per cent. NaOH.

But 1 c.c. 1 per cent. NaOH solution contains ·01 gm. NaOH.

$$\therefore \text{ 20 c.c. unknown acid were neutralised by } 10{\cdot}4 \times {\cdot}01$$

$$= {\cdot}104 \text{ gm. NaOH.}$$

By the equation

$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O$$

80 gm. NaOH neutralise 98 gm. H_2SO_4.

$$\therefore \text{ 20 c.c. unknown acid contain } \frac{{\cdot}104 \times 98}{80} \text{ gm. } H_2SO_4,$$

$$\text{and 1000 c.c. unknown acid contain } \frac{{\cdot}104 \times 98 \times 1000}{80 \times 20} \text{ gm. } H_2SO_4$$

$$= 6{\cdot}37 \text{ gm. } H_2SO_4.$$

But the 10 c.c. of the commercial acid were diluted to 1 litre, so that 10 c.c. of the commercial acid contain 6·37 gm. H_2SO_4, or the strength of the acid is 63·7 gm. H_2SO_4 in 100 c.c.

The percentage of acid sulphate ($NaHSO_4$) contained in a sample of the salt can be similarly determined, if 10 gm. of the solid are weighed out into a litre flask, made up to 1000 c.c., and neutralised as above. The equation representing the reaction is

$$NaOH + NaHSO_4 = Na_2SO_4 + H_2O.$$

177. The Examination of Natural Sulphur Compounds.—

Natural substances which contain sulphur are found in undrained land and also in beds in the Fens and other areas.

Exp. 200.—Roast on crucible lids specimens of iron pyrites, copper pyrites, and realgar. Note any changes, and test any gases you observe.

Many natural ores give off sulphur dioxide when they are roasted in the air, so we may assume that they contain sulphur.

178. The Action of Metals on Sulphur. Sulphides.

Exp. 201.—Mix iron filings with twice their weight of sulphur. Test some of the mixture with dilute sulphuric acid, a magnet, and carbon disulphide (*with great care*, see Exp. 188). Now heat the mixture in a boiling tube or crucible until it is just red-hot. When cool, test by the same three tests again, and also test any gases by lead acetate paper.

We observe that a chemical change has taken place in which the mixture becomes non-magnetic and insoluble in carbon disulphide, and that by the action of dilute sulphuric acid a gas smelling of rotten eggs and blackening lead acetate paper is given off.

The combination of iron and sulphur may be partly represented by an equation in which Fe is the symbol for iron, thus :—

$$\mathrm{Fe} + \mathrm{S} = \mathrm{FeS},$$

where the symbol FeS represents a compound of two substances, iron and sulphur, which, according to our method of naming, is called a *sulphide*, sulphide of iron. This sulphide of iron is generally known as ferrous sulphide.

The energetic character of the combination of metals with sulphur is most easily seen in the case of copper.

Exp. 202.—Make a spiral of copper wire about 3 or 4 cm. long, which will just slip easily into a test-tube containing a few pieces of sulphur. Heat the sulphur until it boils, and note what takes place.

We note that sulphur combines directly with metals, with change of properties and heat changes. As in the case just considered, since the compounds only contain two elements, one of which is sulphur, they are called *sulphides*. The ores of the metals which we have just examined (Exp. 200) are sulphides, and we must proceed to examine more carefully the gases given off by the action of acids upon sulphides.

179. The Action of Acids on Sulphides.

Exp. 203.—Place a few lumps of ferrous sulphide in a gas jar, pour in dilute sulphuric acid, and cover the jar with a glass plate. After a minute or so, remove the plate, and test the gas with a lighted taper. Put back the plate, and when the flame is out allow the jar to fill again and try to pour the gas (i) downwards, (ii) upwards into a clean dry jar; test with a flame and note whether any recognisable products are formed. Fill another jar with the gas, and invert it over water; note its solubility. Examine also the smell of the gas and its action on lead acetate paper.

Note.—The gas may be prepared for examination, if preferred, in the same form of apparatus as carbon dioxide, Exp. 45.

We note that when dilute sulphuric acid is poured upon ferrous sulphide, a colourless gas is given off with a characteristic smell of rotten eggs; it is heavier than air, soluble in water, and burns in air, forming sulphur dioxide, drops of a liquid, and a deposit of sulphur. The liquid is found to be water. Hence we infer that since water is formed when the new gas burns in air the gas must contain hydrogen as well as sulphur; but it may, perhaps, contain oxygen as well.

Exp. 204.—Fit a piece of combustion tube about 20 cm. long with two corks, through which pass single tubes. Place some sulphur in the long tube, and clamp it horizontally. Fit up an apparatus for preparing dry hydrogen, and attach it to one of the tubes. Pass hydrogen through the apparatus until the tube *is free from air,* heat the sulphur, and test the gas which comes out of the other end of the horizontal tube by smell and by lead acetate paper.

We observe that the new gas can be formed by the combination of hydrogen and sulphur only, so that it cannot contain oxygen. It is therefore called *hydrogen sulphide* or *sulphuretted hydrogen.*

It is found that sulphuretted hydrogen contains its own volume of hydrogen, and that it has a molecular weight of 34.

Hence 1 molecule of sulphuretted hydrogen contains 1 molecule, that is, 2 atoms of hydrogen, and as we have already decided to take 32 as the atomic weight of sulphur, the formula becomes H_2S.

We can now represent the preparation of sulphuretted hydrogen from ferrous sulphide by an equation, thus :—

$$FeS + H_2SO_4Aq = FeSO_4Aq + H_2S.$$

180. The Properties of Sulphuretted Hydrogen.—Some of the properties of hydrogen sulphide and of its solution in water are of very great importance in chemistry.

Exp. 205.—Pass sulphuretted hydrogen through a wash bottle containing water, and then through distilled water, until a saturated solution is made. Taste the solution, and test it with litmus. Make solutions of copper sulphate and lead acetate in water and arsenic in hydrochloric acid, and add some of the solution of the gas to each. Note the appearance and colours of the precipitates. Filter off and wash the precipitates and test them by hydrochloric acid; note whether they give off sulphuretted hydrogen or not.

Sulphuretted hydrogen solution is slightly acid and gives precipitates with solutions of many metals. These precipitates are found to be sulphides, which have in many cases characteristic properties by which they may be recognised.

Exp. 206.—Pass sulphuretted hydrogen through (i) chlorine water, (ii) nitric acid, (iii) potassium permanganate solution acidified with hydrochloric acid, and (iv) sulphurous acid. Note any changes. Test for hydrochloric acid by litmus and by silver nitrate solution in (i), and test for sulphuric acid by barium chloride and hydrochloric acid in (ii) and (iii), filtering when necessary.

We note in (i) that hydrochloric acid is formed with a deposit of sulphur, in (ii) that nitrous fumes are formed with a deposit of sulphur, in (iii) that the solution is decolorised with the formation of sulphuric acid and deposit of sulphur, and in (iv) that sulphur is deposited.

Reaction (i) reminds us of the bleaching action of chlorine, in which the chlorine removes hydrogen from water, forming hydrochloric acid and setting oxygen free. In (ii) and (iii) part of the gas is oxidised to sulphuric acid, at the expense of the oxygen of the other reacting substance, so that the gas is able to act as a reducing agent. In (vi) we observe the curious interaction of an oxide and a hydride of the same element, resulting in the formation of the free element and water, together with other complicated products which do not concern us; the change, however, is one which probably occurs in nature and results in the deposit of sulphur in the soil of volcanic areas.

Undrained waterlogged clay and fen land sometimes contain sulphuretted hydrogen, as tested by the smell and lead acetate paper, and this gas is poisonous to plant life. Such soil is generally bluish in colour and gradually becomes redder on exposure to the air, losing the sulphuretted hydrogen. This is due to gradual oxidation and also to interactions between the oxide and hydride as in (iv), and the final result appears to be the formation of sulphuric acid which may appear as gypsum (see Art. 217).

CHAPTER XV.

SODIUM, POTASSIUM, AND AMMONIUM COMPOUNDS.

181. Compounds of Sodium, Potassium, and Ammonium.—Many of these compounds are of importance in agriculture, and will now be considered in detail.

182. Common Salt.—The commonest and most plentiful sodium compound is common salt, which is found as rock salt in various parts of the world, notably in this country in Cheshire. Common salt is also found dissolved in sea-water, and in salt springs in various places. The salt is purified by dissolving it in water, filtering the solution or allowing impurities to settle, and crystallising out the pure substance. As prepared in this way it is a colourless solid with a characteristic taste, it is soluble in water, and melts at a high temperature. Unless very pure, salt tends to become damp in wet weather.

The amount of any salt which can be dissolved by a given quantity of water is of importance.

> **Exp. 207.**—Put into a flask some common salt and distilled water. Shake well, adding more salt if necessary, until some is left undissolved, and allow the mixture to stand for some time. Read its temperature, pipette off 20 c.c. of the solution into a weighed evaporating basin, and evaporate over a water bath until the salt loses no more weight.

The weight of the residue is the weight of salt dissolved in 20 c.c. of the solution, and hence the weight dissolved in 100 c.c. of the solution can be found.

This value is generally useful in chemistry, but since the dissolved solid takes up some room, it is usual to calculate the result in such a way as to allow us to compare the different weights of salt dissolved by the same weight of water, *i.e. the solubility in water* of the salt examined.

Exp. 208.—Weigh a dry basin, note the temperature of the solution prepared as in the previous experiment, pour about 20 c.c. of the solution into the basin, and weigh again. Evaporate over a water bath until the weight is constant, and weigh again.

We may take an example :—

Weight of basin and solution = 83·61 gm.
,, ,, ,, = 59·79 gm.
,, ,, solution = 23·82 gm.

Weight of basin and residue = 66·07 gm.
,, ,, ,, = 59·79 gm.
,, ,, residue = 6·28 gm.

That is, 23·82 gm. of solution contain 6·28 gm. of salt, or, subtracting, 23·82 – 6·28 = 17·54 gm. of water dissolve 6·28 gm. of salt. Hence 100 gm. of water dissolve 35·8 gm. of salt.

Exp. 209.—Repeat the last experiment, but keep the flask on a water bath all the time the salt is dissolving. Weigh out about 20 c.c. of the hot solution as before, noting its temperature, and calculate the solubility again. Note whether there is any difference between the two values obtained.

We observe that the solubility of a salt has different values at different temperatures, so that in stating the solubility it is necessary to give the temperature at which the solution has been made. A solution which, at any temperature, contains all the salt which it can hold at that temperature is said to be *saturated.* The temperatures of the two solutions in Exps. 208 and 209 should be stated in your results.

We also note that there is not a very great difference between the solubilities of common salt at low and at high temperatures.

[*Note.*—Other good and simple methods of determining solubilities can be used.]

183. Sodium.—Common salt is the commonest compound of sodium which can easily be obtained in a pure state, and most other sodium compounds are prepared from it. The methods by which these compounds are prepared are of enormous commercial importance, but are not generally suitable for laboratory use. Certain preparations are, however, of agricultural interest, and we may consider modern methods based on the application of electricity to chemistry as sufficient for our purpose.

When an electric current is passed through molten common salt the salt is split up into sodium and chlorine, and if the electrolysis is carried out in a **U**-tube the two products can be separated. The chlorine is led away and the sodium is cast into sticks, and is useful in many chemical reactions.

The equation representing the electrolysis is

$$2NaCl = 2Na + Cl_2.$$

Exp. 210.—Examine a piece of sodium, cut it, examine the cut face. Heat a little piece on a piece of iron in a flame. [Be very careful to keep the metal away from water.]

Sodium is a soft, silvery metal, which tarnishes rapidly in moist air. As we have seen, it decomposes water, forming the hydroxide $NaOH$, caustic soda (Exp. 148) and also combines with chlorine forming the chloride $NaCl$ (Exp. 125). It burns in air with a yellow flame and forms an oxide represented by the formula Na_2O, called *sodium monoxide*, or a mixture of this oxide with another represented by Na_2O_2, and called *sodium peroxide.*

184. Caustic Soda.—Sodium reacts with water to form caustic soda, and methods of preparing this substance have been based on bringing the sodium as it is formed by electrolysis into contact with water or steam.

In the former case, the electrolysis of the solution of the sodium compound is carried out in tanks divided into compartments in such a way that the liberated sodium is dissolved in mercury and carried into a part of the tank containing pure water, where the formation of the caustic soda solution takes place : this solution is evaporated to dryness.

In the latter case, the current passes through the fused salt floating on molten lead in one compartment of a tank, and the dissolved sodium is carried by the lead to another compartment where it decomposes steam, and caustic soda is obtained in the melted state.

Caustic soda comes on the market as sticks or a powder, and in the latter case may be of nearly 100 per cent. purity.

Exp. 211.—Examine a specimen of caustic soda. Place a small piece on a glass plate in the air. Put a small piece on paper and moisten it. Make a solution and test with litmus, copper sulphate, and silver nitrate solutions. [Be careful not to handle the solid.]

Caustic soda is a white solid, which rapidly becomes moist in the air by taking up water, *i.e.* it is *deliquescent.* It is very soluble in water and rapidly acts on paper, making it swell and become gelatinous: similarly it eats away the skin and it is therefore said to be caustic. It gives a blue gelatinous precipitate with copper sulphate, of great importance to potato growers (see Art. 251), and a brown precipitate with silver nitrate. The precipitates given with caustic soda are generally hydroxides, and in the above cases are represented by the formulae $Cu(OH)_2$ and $AgOH$ respectively. On boiling the copper solution the precipitate turns black; this will be referred to again later.

Exp. 212.—Shake up some caustic soda solution with olive oil or suet.

The solution gradually forms a froth from the formation of soap.

185. Sodium Sulphate.—We have already examined the action of sulphuric acid on common salt in the preparation of hydrochloric acid, and we have examined the reactions between caustic soda and sulphuric acid which result in the formation of the two sodium sulphates. Apart from the action of the electric current the former reaction is the only convenient one for obtaining other sodium compounds from common salt; it takes place in two stages, which we may represent by equations:—

$$2NaCl + H_2SO_4 = NaCl + NaHSO_4 + HCl \text{ (in the cold)}$$
$$= Na_2SO_4 + 2HCl \text{ (when heated)}$$

Sodium sulphate forms large colourless crystals when its solution is evaporated; these are commonly called *Glauber's salt.*

Exp. 213.—Examine some crystals of sodium sulphate. Heat some of the crystals in a test-tube, and note the products. Into a weighed crucible place about 2 gm. of sodium sulphate crystals, heat gently at first, and finally to a red heat. Weigh again and note the percentage of loss.

Suppose the loss of weight amounted to 56·0 per cent. This loss of weight is due to the loss of water alone, and we can calculate a formula for the crystalline salt if we represent the dry salt by the formula Na_2SO_4. We calculate the weight of water which combines with the formula weight of sodium sulphate *i.e.* with $(46 + 32 + 64 = 142$ gm.). Using the above result, since 56 gm. of water combine with $(100 - 56) = 44$ gm. of sodium sulphate, Na_2SO_4, therefore 142 gm. of the salt combine with $\frac{142 \times 56}{44} = 181$ gm. of water. Now since one molecular weight of water weighs 18 gm., the loss of water corresponds with $\frac{181}{18}$ molecular weights of water $= 10H_2O$, so that the formula of the crystalline salt is $Na_2SO_4, 10H_2O$. Water which combines in this way with a salt to form a crystalline solid is called *water of crystallisation.*

Examine crystals of sodium sulphate which have been exposed to the air for some time. They are covered with a white powder and may be shown to contain less water than the transparent crystals: such crystals which lose water on exposure to air are said to be *efflorescent.*

186. The Preparation and Properties of the Carbonates of Sodium.—Having once prepared sodium sulphate from common salt we can change it into sodium sulphide, Na_2S, by the removal of oxygen: this is brought about by heating the substance with carbon, and the sulphide is further changed to carbonate by the action of chalk. Sodium sulphate, carbon, and chalk are all heated together in a furnace and then the product is digested with water. The solution on evaporation yields crystals, and the residual calcium sulphide is treated to regain the sulphur it contains. The whole process is called the *black ash* process, and equations may be written to represent the changes:—

$$Na_2SO_4 + 4C = Na_2S + 4CO,$$

$$Na_2S + CaCO_3 + Aq = Na_2CO_3Aq + CaS.$$

The solution deposits, on evaporation, colourless crystals, called commercially soda or *soda crystals.*

Exp. 214.—Examine some soda crystals by the action of water, heat, litmus solution, and hydrochloric acid, testing the gas given off by lime water.

The crystals are soluble in water, alkaline to litmus, and contain carbon dioxide, and they give off water on heating. When free from water they are represented by the formula Na_2CO_3.

Exp. 215.—Repeat Exp. 213 with crystals of sodium carbonate instead of the sulphate, and calculate the number of molecular weights of water which combine with one formula weight (= 106 gm.) of sodium carbonate.

The number of molecular weights is found to be 10, so that sodium carbonate crystals are represented by the formula Na_2CO_3, $10H_2O$.

Carbonates are compounds essential to living matter, and must be carefully investigated.

Sodium carbonate contains two atoms of sodium in its formula, and we may try whether these can be replaced by hydrogen.

Exp. 216.—Make a saturated solution of sodium carbonate; pass carbon dioxide through a wash bottle containing water, in order to wash it, and then into the solution. Collect the solid formed, and dry it by means of blotting-paper. Test it by acids and the action of heat; identify the products.

We have prepared another solid carbonate of sodium, which on heating gives off carbon dioxide as well as water, and leaves sodium carbonate behind.

We may infer from our observations on the sulphates that this carbonate may be represented as a hydrogen carbonate, *sodium hydrogen carbonate* or *sodium bicarbonate*, in which case it should be represented by the formula $NaHCO_3$. Its decomposition by heat might then be represented by the equation

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

To confirm this we can investigate quantitatively the action of heat upon the salt.

Exp. 217.—Weigh about 2 gm. of sodium bicarbonate in a weighed crucible, and heat it to redness. Find the loss of weight per cent.

Now, if our supposition is correct, this loss of weight is due to the loss of both water and carbon dioxide; the loss of carbon dioxide alone can be found by noting the loss of weight after absorbing the water by calcium chloride.

Exp. 218.—Fit a test-tube with a cork and calcium chloride tube, either straight (Fig. 81) or U-shaped, and weigh it. Put in about 2 gm. of sodium bicarbonate and weigh again. Now heat the salt until the weight is constant, and find the percentage loss, which consists of carbon dioxide only.

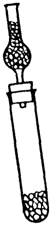

Fig. 81.

We have now obtained numbers from which we can calculate the percentage composition of the salt.

To take an example :—

2 gm. salt lose 0·74 gm. on heating = 37%

2 gm. salt lose 0·53 gm. (as dry CO_2) on heating with calcium chloride = 26%

∴ percentage of water = 11

The percentage composition may be represented thus :—

Sodium carbonate	=	63
Carbon dioxide	=	26
Water	=	11
		100

We have decided to represent sodium carbonate by Na_2CO_3, with a formula weight of 106 ; so that we calculate from the above data the amount of water and of carbon dioxide which are combined with 106 gm. sodium carbonate. The results to the nearest whole number are :—

$$Na_2CO_3 = 106$$
$$CO_2 = 44$$
$$H_2O = 18$$

The proportions of the molecules of sodium carbonate, carbon dioxide, and water are therefore

$$Na_2CO_3 : CO_3 : H_2O = \tfrac{106}{108} : \tfrac{44}{44} : \tfrac{18}{18} = 1 : 1 : 1,$$

so that the formula of the compound is built up of

$$Na_2CO_3 + CO_2 + H_2O = Na_2H_2(CO_3)_2 \text{ or } 2NaHCO_3.$$

It is really a *bicarbonate of sodium* corresponding with the carbonate Na_2CO_3.

We can make a further inference, viz. that since we can prepare both carbonates and bicarbonates, they must be derived from an acid, *carbonic acid*, which can be represented by the formula H_2CO_3, in which case the common sodium carbonate Na_2CO_3 is the normal carbonate, and the bicarbonate $NaHCO_3$ is the acid carbonate or hydrogen carbonate.

We may now compare the two carbonates.

Exp. 219.—(i) Examine the action of heat on both carbonates, (ii) make a solution of both carbonates in cold water, and test by (*a*) litmus, methyl orange, and phenol phthalein, (*b*) boiling and testing the gases given off, (*c*) magnesium sulphate solution, (*d*) silver nitrate solution, (*e*) mercuric chloride solution.

From these reactions we observe (i) that the normal carbonate is not decomposed by heat while the acid carbonate is and yields carbon dioxide and steam, and that the acid carbonate is also partly decomposed by boiling in water ; (ii) that both the normal and the acid carbonates are alkaline to litmus and to methyl orange, while the normal carbonate is alkaline and the bicarbonate neutral to phenol phthalein ; (iii) that the normal carbonate gives a white precipitate with magnesium sulphate, a yellowish white precipitate with silver nitrate, and a red precipitate with mercuric chloride, while the acid carbonate gives no precipitate with magnesium sulphate and only a white turbidity with silver nitrate and mercuric chloride.

We have now tests to distinguish between a hydroxide, a carbonate and a bicarbonate, since with a hydroxide silver nitrate gives a brown precipitate and mercuric chloride a yellow, with a carbonate silver nitrate gives a whitish precipitate and mercuric chloride a red, and with a bicarbonate neither reagent gives a precipitate until boiled, when the carbonate precipitate appears.

187. The Estimation of the Carbonates of Sodium.—In Exp. 219 we noted that normal sodium carbonate is alkaline to all indicators, while sodium bicarbonate is neutral to phenol phthalein.

Exp. 220.—Heat some dry sodium carbonate (B.P.) in a porcelain crucible and allow it to cool in a corked flask or desiccator. Weigh out 5 gm. when cool and dissolve in a 500 c.c. flask, making up to the mark. Pipette off 20 c.c. of the 1 per cent. solution, and neutralise with 1 per cent. hydrochloric acid, using methyl orange as an indicator. [Note.—Litmus may be used if the solution is boiled after each colour change.]

Supposing the neutralisation requires a mean of 13·8 c.c. of 1 per cent. HCl solution, the results can be examined as follows :—

20 c.c. of 1 per cent. sodium carbonate solution contain ·2 gm. Na_2CO_3, and 13·8 c.c. of 1 per cent. HCl solution contain ·138 gm. HCl.

That is, ·2 gm. Na_2CO_3 neutralise ·138 gm. HCl, or 105·8 gm. Na_2CO_3 neutralise 73 gm. HCl.

We can write an equation to represent this relation—

$$Na_2CO_3 + 2HCl = H_2O + 2NaCl + CO_2,$$

and this equation will represent quantitatively the reaction which takes place.

It appears, therefore, that sodium carbonate solution neutralises acids as if it contained an equivalent quantity of caustic soda (2NaOH), so that it is often used in estimations instead of that reagent.

Exp. 221.—Repeat the previous experiment, using phenol phthalein as an indicator instead of methyl orange.

It is found that about 6·9 c.c. of 1 per cent. HCl solution are sufficient to neutralise 20 c.c. of the 1 per cent. Na_2CO_3 solution to phenol phthalein. The observation that sodium bicarbonate is neutral to this indicator enables us to represent the reaction quantitatively by the equation

$$Na_2CO_3 + HCl = NaHCO_3 + NaCl.$$

Since the solution is now neutral to phenol phthalein it is colourless, and on the addition of methyl orange the remainder of the soda can be estimated by the addition of 1 per cent. HCl solution in the usual way. The method of using two indicators in succession is often useful in commercial analyses.

188. The Preparation of Caustic Soda.—We have already noted the preparation of caustic soda direct from common salt by the electrolysis of its solution in water; another older preparation is of great interest and commercial importance.

Exp. 222.—Take 30 gm. of soda crystals and place them in a small iron saucepan with 300 c.c. of water and 10 gm. of slaked lime. Boil for some time, keeping the water made up to about 300 c.c., until a few drops of the liquid when filtered do not fizz on the addition of hydrochloric acid. When this is the case, filter, evaporate half the filtrate to dryness, and keep the other half. Test the solid residue for carbonates and the solution for caustic soda as in Exp. 211.

We note that when sodium carbonate is boiled with slaked lime in dilute solution, calcium carbonate is precipitated and white soluble sodium hydroxide, caustic soda, NaOH, is formed.

The reaction can be represented in the form of an equation,

$$Ca(OH)_2Aq + Na_2CO_3Aq = CaCO_3 + 2NaOHAq,$$

in which we distinguish between a substance in solution and an insoluble solid by the use of the symbol Aq as part of the formula of the dissolved substance. (See also Art. 131(*c*)). The above equation will thus tell us that when solutions of slaked lime and sodium carbonate are mixed, a precipitate of insoluble chalk is formed, while caustic soda remains in solution.

189. Sodium Nitrate. Estimation of Common Salt.—Sodium nitrate has already been examined (Chapter XI). As a manure, it is a most important source of nitrogen, but it is apt to take up water from moist air, *i.e.* to *deliquesce* in moist air, especially if impure. It may further contain common salt as an impurity, and as common salt has a very low price compared with the nitrate it is sometimes used to adulterate the nitrate.

The presence of common salt may be detected by the test for hydrochloric acid and chlorides which we found in Exp. 116. This reaction may be examined quantitatively to see if it can be used for the estimation of common salt.

Exp. 223.—Weigh out 10 gm. of pure crystallised silver nitrate, dissolve it in distilled water and make it up to 1 litre with distilled water. Also make up 250 c.c. of a 1 per cent. solution of pure sodium chloride in the usual way.

Measure out 10 c.c. of the 1 per cent. NaCl solution into a perfectly clean stoppered bottle and add the standard silver nitrate solution from a burette, 5 c.c. at a time, shaking well after each addition. The liquid is at first rendered milky by each 5 c.c., but the time comes when the precipitate settles, and no further milkiness is seen. Now repeat, using 1 c.c. only as the precipitate begins to settle, and finally repeat, using ·1 c.c. at a time.

The result comes out about 29·1 c.c. It is, however, more convenient and rather quicker to use a colour change to show the end of a reaction.

Exp. 224.—Measure out 10 c.c. of the 1 per cent. NaCl solution into a porcelain basin and add 2 or 3 drops of a solution of potassium chromate to colour the liquid a pale yellow. Now run in the standard silver nitrate solution, stirring with a glass rod, firstly until a red colour is produced, and then more carefully until only an orange tint is seen.

The result comes out about 29·1 c.c., exactly as in the previous experiment, so that potassium chromate can be used as an indicator instead of the absence of the formation of a precipitate, and the reaction is quantitative.

Since the formula weight of common salt, NaCl, is 58·5, the amount of silver nitrate, which is represented by the formula $AgNO_3$, required to precipitate a formula weight of common salt is $\frac{58{\cdot}5 \times {\cdot}291}{{\cdot}1} = 170$ gm. Now 170 represents the formula weight of silver nitrate if the atomic weight of silver is 108, so that the equation representing the precipitation may be written

$$\underset{58{\cdot}5\text{ gm.}}{NaCl} + \underset{170\text{ gm.}}{AgNO_3} = \underset{85\text{ gm.}}{NaNO_3} + \underset{143{\cdot}5\text{ gm.}}{AgCl},$$

Exp. 225.—Weigh out 10 gm. of commercial Chile saltpetre, dissolve and make up to 250 c.c. Pipette off 20 c.c. at a time into a basin, add a few drops of potassium chromate solution and run in 1 per cent. silver nitrate solution until the colour just changes to orange.

Supposing that 11 c.c. is the mean of the estimations of the number of c.c. of the 1 per cent. silver nitrate taken.

Then 11 c.c. 1 per cent. $AgNO_3$ solution contain ·11 gm. $AgNO_3$, and from the above equation 170 gm. $AgNO_3$ precipitate 58·5 gm. NaCl.

$\therefore$ 11 c.c. 1 per cent. $AgNO_3$ precipitate $\frac{{\cdot}11 \times 58{\cdot}5}{170}$ gm. NaCl.

But this is contained in 20 c.c. of the nitrate solution, so that 250 c.c. of the solution, containing 10 gm. of the salt contain $\frac{{\cdot}11 \times 58{\cdot}5}{170} \times \frac{250}{20}$ gm. NaCl $=$ ·47gm. NaCl, and the percentage of common salt $= \frac{{\cdot}47 \times 100}{10} = 4{\cdot}7$.

Since 58·5 gm. of common salt contain 35·5 gm. of chlorine, and 170 gm. of silver nitrate contain 108 gm. of silver, we can also use the above method to estimate the percentage of chlorine in a solution or a solid body, calculating on the basis that 170 gm. of silver nitrate or 108 gm. of silver precipitate 35·5 gm. of chlorine.

190. Tests for Sodium Compounds.—Sodium compounds are very widely distributed in soils, plants, and animals, so that the colouring of a flame yellow is not a perfectly satisfactory test for their presence in varying quantity. All the common sodium salts, too, are soluble in water, so that we cannot make the formation of a precipitate with any reagent into a test for the presence of sodium. We are, in fact, reduced to removing of all other metals by ammonium salts, evaporating the filtered solution to dryness and driving off the ammonium salts by heat : if no residue is left, then no appreciable quantity of sodium salts was originally present, but if there is a residue which turns the flame bright yellow, we may infer the presence of sodium salts.

191. Potassium Compounds. The Carbonates of Potassium.

Exp. 226.—Burn some pieces of wood, or, better, collect the ashes of a wood fire or bonfire and boil them with water. Filter and evaporate the solution to dryness. Test the white solid left by the flame, litmus, acids, mercuric chloride, silver nitrate, etc.

We find that wood ashes contain a soluble white solid, which is a carbonate and colours the flame lavender ; it is therefore a carbonate of the metal potassium. This carbonate of potassium is the normal carbonate, and crystallises from solution in crystals represented by the formula $2K_2CO_3, 3H_2O$ or $K_2CO_3, 1\frac{1}{2}H_2O$, but on being heated to above 130° C. it loses the water and is represented by the formula K_2CO_3. Potassium carbonate, as prepared in the above manner, is sold as *potashes* or *pearlash*.

Potassium compounds are contained in the ashes of all land plants, and potassium is one of the elements which are essential to plant life and growth. It is obtained by plants from the soil, in which it exists in small quantities derived from the rocks from which the soil is formed; in the rocks it is contained in the form of felspar (orthoclase felspar).

The potassium compounds contained in plants used as food pass into the animal body and form essential constituents of milk and other secretions. They are also excreted through the skin, and in the case of sheep are retained by the wool in the form of a fat or grease. This grease burns and leaves a residue of potassium carbonate which has considerable value.

Since we can prepare potassium carbonate direct from wood ash, we need not here consider any other method of preparation, so that the study of the potassium compounds is simpler than that of the sodium compounds.

Potassium carbonate is very soluble in water, 100 gm. of water dissolving 95 gm. of the salt, and when carbon dioxide is passed through the solution the much less soluble bicarbonate, $KHCO_3$, separates out. The bicarbonate crystallises from water in large crystals, having the formula $KHCO_3, H_2O$.

The properties of the carbonates of potassium are similar to those of the sodium carbonates, and they can be estimated in solution by standard acid solutions, as in Exps. 220 and 221.

The bicarbonate is crystalline, so that it can be used as a standard solid for making standard alkali solution.

Since the carbonate of potassium is soluble in water it is advisable, when using the ashes of fires burning vegetable matter for manure, to spread the ashes before rain falls on them.

192. Caustic Potash.—Caustic potash, KOH, can be prepared in the same way as caustic soda, which it much resembles. It precipitates hydroxides from solutions of other metallic salts, and is very soluble in water.

The metal *potassium*, K, is also prepared in a similar way to sodium and has similar properties. It is a soft, white metal, which reacts with water forming the hydroxide.

193. Potassium Chloride.—Potassium chloride, called commercially muriate of potash, is not so commonly found in quantity as sodium chloride. It is nearly twice as soluble in hot water as the sodium salt, and when the salt lagoons were gradually drying up and depositing rock salt, the potassium salt appears to have concentrated and to have been deposited on the top of the rock salt; sometimes it has been washed away. The potassium chloride is, however, found in quantity in many places, especially over the salt beds at Stassfurth in Germany and in Alsace. It is also found in these salt beds with sulphates and chlorides of magnesium and sodium, and is crystallised out from concentrated solutions in a nearly pure state.

When pure, potassium chloride is a colourless crystalline substance without water of crystallisation, and is represented by the formula KCl. Its less pure commercial forms are coloured and are sold according to the percentage of potassium they contain under the name of *kainit.*

Potassium chloride acts in a similar manner to common salt, and other potassium compounds are prepared from it commercially just as the corresponding sodium compounds. For laboratory purposes the natural carbonate or caustic potash is the most convenient source of potassium.

194. Potassium Sulphate.—Potassium sulphate is often used as a manure instead of the chloride, which destroys the texture of some soils and affects the quality of some crops. It is generally prepared from the chloride by the action of sulphuric acid, and it crystallises in hard, colourless prisms, without water of crystallisation, and represented by the formula, K_2SO_4; it is not very soluble in water.

195. Potassium Nitrate.

Exp. 227.—Make saturated solutions of Chile saltpetre (sodium nitrate) and potassium chloride in boiling water, and mix about equal volumes of the boiling solutions. Filter (if necessary) while hot and allow the mixture to cool. Examine the crystals which separate out, and compare them with the original salts. Pour off the liquor, collect the long crystals formed, and dry them by blotting-paper. Test them by a flame, by strong sulphuric acid, and by ferrous sulphate and strong sulphuric acid as in Exp. 141.

We note that when hot saturated solutions of potassium chloride and sodium nitrate are mixed and cooled, long crystals of potassium nitrate, KNO_3, saltpetre or nitre, crystallise out; a few small cubical crystals of common salt, NaCl, are often formed.

This reaction is interesting as giving us a method of preparing a salt by mixing two other salts. Since both of the original salts are decomposed the method is called the method of *double decomposition.* The following equation represents part of the reaction, viz. the final products:—

$$NaNO_3 + KCl = KNO_3 + NaCl.$$

The explanation of this change is very interesting, and is based on the fact that common salt is nearly as soluble in cold water as in hot, while all the other salts are more soluble in hot water than in cold; consequently when the hot saturated solutions are mixed, though a little sodium chloride is precipitated, the greater part remains in solution on cooling while on the other hand the potassium nitrate which is much less soluble in cold water than in hot, crystallises out.

Potassium nitrate is important on account of the large proportion of oxygen which it contains and which it can give up in the oxidation of other substances.

Exp. 228.—Melt a few crystals of potassium nitrate in a test-tube. Make a small piece of charcoal red-hot and drop it into the fused nitrate. Note the effect.

Exp. 229.—Mix $7\frac{1}{2}$ gm. of powdered saltpetre, $1\frac{1}{2}$ gm. of charcoal, and 1 gm. of sulphur carefully in a mortar, pile it up on an empty sand bath, and light it with a taper. Note the rapid combustion.

* **Exp. 230.**—(*Demonstration Exp.*) Make a paper tube, close up one end tightly, and ram some pieces of paper into it. Then fill the tube with the above composition, ramming the mixture in with a pencil or rod.

Grip with a pair of tongs, light the mixture at the open end of the tube, and plunge the tube, open end down, into a pail or bowl of water. Collect the gaseous products in a large gas jar.

We note that potassium nitrate causes charcoal and a mixture of charcoal and sulphur to burn when lit, and that the burning does not require oxygen from the air, since the mixture will burn under water. We note that the volume of gas produced is many times larger than the original volume of the mixture, so that if the gases are not allowed to expand they will produce a very high pressure in the containing vessel. This pressure is used for the propulsion of shot and bullets from guns, and the mixture we have prepared forms *gunpowder*.

196. Potassium Chlorate.—We have seen that a metal and its oxide and hydroxide all form the same salt, a chloride, when dissolved in hydrochloric acid, and that the same chloride is formed by direct combination of the metal and the radicle of the acid, viz. chlorine ; we may lastly examine the action of the radicle chlorine on the base of the metal.

Exp. 231.—(*To be done in the draught chamber.*) Take about 20 c.c. of water in a beaker, and dissolve in it a stick (about 10 gm.) of caustic potash. Pass chlorine into the liquid, using a funnel as in Exp. 117. When the liquid no longer dissolves the gas readily, warm it, and continue to pass chlorine until no more is dissolved. Evaporate the solution until a drop of the hot liquid suspended on a glass rod shows crystals on cooling, and then allow the whole to cool. Filter off any crystals which may be formed, wash them quickly on the filter paper by pouring cold water on them, and dry them by standing on a pad of blotting paper under an inverted funnel. Evaporate the rest of the solution to dryness over a water bath, when a second crystalline substance will be obtained. Roughly weigh both quantities of solids and test them by (i) heating in a small test tube, (ii) adding one drop of concentrated sulphuric acid to one small crystal in a test-tube and warming gently (N.B.—This experiment must be done very carefully with the open end of the test-tube pointing away from the operator), and (iii) heating in the flame.

We notice that chlorine dissolves in a hot strong solution of caustic potash, forming two different white crystalline substances. One we recognise as a chloride, potassium chloride, the other gives off oxygen when heated alone, and turns brown with strong sulphuric acid, exploding when warmed. About three times as much of the chloride is formed as of the other solid, which is *potassium chlorate.*

There appears to be a great difference between the reactions of caustic potash with chlorine and with hydrochloric acid, since in the former case we obtain an oxygen compound, potassium chlorate, as well as potassium chloride, while in the latter case we obtain the chloride of potassium only.

An equation can be used to represent the latter reaction—

$$6KOH + 3Cl_2 = 3H_2O + 5KCl + KClO_3.$$

Exp. 232.—Heat a few crystals of potassium chlorate to redness in a test-tube. Test both the product and a small crystal of unheated chlorate with silver nitrate solution, as well as with strong sulphuric acid and with the flame test.

Potassium chlorate appears to be converted into potassium chloride by the action of heat, oxygen being given off, and this reaction may be used to find the composition of the former salt.

It is found that 100 gm. of the chlorate yield about 40 gm. of oxygen and 60 gm. of potassium chloride, and these figures agree with a formula $KClO_3$ as representing potassium chlorate, and the equation

$$2KClO_3 = 2KCl + 3O_2.$$

as representing the decomposition of potassium chlorate by heat.

The explanation and representation of the action of manganese dioxide on the decomposition of potassium chlorate (see Exp. 29) is somewhat complicated, but we can express the fact that it is apparently unchanged at the end of the reaction, thus :—

$$2KClO_3 + MnO_2 = 2KCl + 3O_2 + MnO_2.$$

A substance which affects the conditions under which a chemical reaction takes place without altering the final products is generally called a *catalyst* or *catalytic agent*, and the manganese dioxide is here a catalytic agent.

197. Tests for Potassium Compounds.—Potassium compounds are so important for plant life that we require a test for them ; they are not so plentiful as sodium compounds and are applied as manures.

Exp. 233.—To a solution of potassium chloride add (i) hydrochloric acid and platinum chloride and a little alcohol, (ii) acetic acid and sodium cobaltinitrite solution (de Koninck's reagent). Test a crystal of the salt in a flame.

We note that potassium compounds give a bright yellow precipitate with platinum chloride, insoluble in alcohol, and that they give a yellow precipitate with sodium cobaltinitrite ; they also colour the flame lavender. Ammonium compounds also give similar precipitates with (i) and (ii), so that they must be driven off by heating before the tests are applied, if the tests are to be certain.

198. Ammonium Salts.—In Chapter XIII. we found that ammonia gas combines with acids to form solid bodies ; these resemble the sodium and potassium salts formed from the same acids.

Exp. 234.—Compare the sulphate and chloride of ammonium with those of sodium and potassium. Compare the action of a solution of ammonia with one of caustic soda on litmus, copper sulphate solution, etc.

It is seen that

$NH_3 + HCl$ or NH_4Cl resembles $NaCl$ and KCl

$2NH_3 + H_2SO_4$ or $(NH_4)_2SO_4$,, Na_2SO_4 and K_2SO_4

$NH_3 + H_2O$ or NH_4OH ,, $NaOH$ and KOH.

All three formulae representing the ammonia compounds resemble the corresponding sodium and potassium formulae, but instead of containing atoms of a metal in their formulae they contain a group consisting of 1 atom of nitrogen and 4 atoms of hydrogen, written NH_4. This group contains the hydrogen contained in the ammonia plus that contained in the acid, and appears to be able to act like a metallic atom in the formation of salts.

Such a group of atoms which is able to play the part of a single atom is called a *compound radicle* (radical), or *radicle* (radical) only; the group (NH_4) is termed the *ammonium group*, and sal ammoniac is therefore called ammonium chloride. The ammonium group cannot, unfortunately, be examined, as it easily splits up into ammonia and hydrogen, but we can examine one of its properties.

* **Exp. 235.**—(*Demonstration Exp.*) Take a small quantity of mercury in a mortar and put into it half a dozen very small pieces of sodium, about the size of a split pea, one at a time, squeezing each piece below the mercury with the pestle : note the violent action. The resulting pasty liquid is a solution of sodium in mercury, or *sodium amalgam*. Take a saturated solution of sal ammoniac, and drop into it some of the sodium amalgam. Note the reaction and examine the products.

We see that the sodium disappears and is found in the solution as sodium chloride, while the pasty metallic mass first formed soon splits off ammonia and hydrogen; it appears to be quite metallic, and probably at first contains ammonium in solution. It is termed *ammonium amalgam*.

Ammonia solution acts similarly to caustic soda solution, and thus probably contains a hydroxide resembling caustic soda, NaOH, since it is alkaline to litmus, neutralises acids forming salts, and precipitates hydroxides from solution. We give this compound the formula $(NH_4)OH$, which suggests both its mode of formation and its properties.

$$NH_3 + H_2O = (NH_4)OH.$$

199. Sulphate of Ammonia.—Sulphate of ammonia or ammonium sulphate, represented by the formula $(NH_4)_2SO_4$, is the most important agricultural compound of ammonia. It is obtained in the important industries in which coal and oil shale are heated to redness for the preparation of coal gas and paraffin oils. The gases are liberated in horizontal or vertical tubes or retorts, made of fire-clay in the case of coal, or fire-brick in the case of oil shale, and the red-hot gases are led upwards through towers down which water is sprinkled. The water absorbs the ammonia while it cools the gases. The washing water (gas liquor) is now treated either (*a*) by the old method of neutralising with sulphuric acid and concentrating until crystals are formed, or (*b*) by heating with lime, when the ammonia is expelled and passed into a solution of sulphuric acid from which crystals separate without evaporation.

The second method yields a much purer product and the crystals obtained are colourless instead of yellow as are those obtained in the older process.

The commercial value of the sulphate of ammonia depends on the percentage of ammonia as well as on the absence of impurities, and we can estimate the ammonia by various methods.

200. Estimation of Ammonia in Sulphate of Ammonia Crystals.—If the crystals are neutral to litmus we can proceed as follows :—

Exp. 236.—Make a 1 per cent. solution of the salt as in previous experiments. Pipette off portions of 20 c.c. into beakers, add to each from a burette 40 c.c. of 1 per cent. NaOH solution and boil until the steam no longer turns litmus paper blue. Now neutralise the residue with 1 per cent. HCl solution from a burette, using either litmus or methyl orange as an indicator.

Suppose the average number of c.c. of 1 per cent. HCl required to neutralise the excess of caustic soda was found to be 26·7.

Now

26·7 c.c. of 1 per cent. HCl contain ·267 gm. HCl,

and from the equation

$$HCl + NaOH = NaCl + H_2O$$

40 gm. of NaOH neutralise 36·5 gm. of HCl.

$\therefore$ 26·7 c.c. of 1 per cent. HCl neutralise $\frac{26 \cdot 7 \times 40}{36 \cdot 5}$

$= 29 \cdot 2$ c.c. of 1 per cent. NaOH.

But 40 c.c. of 1 per cent. NaOH were taken,

$\therefore$ $40 - 29 \cdot 2 = 10 \cdot 8$ c.c. of 1 per cent. NaOH solution, containing $10 \cdot 8 \times \cdot 01 = \cdot 108$ gm. NaOH, displaced the ammonia from 20 c.c. of the 1 per cent. solution of ammonium sulphate.

The equation representing this displacement when the ammonia is driven off by boiling is

$$(NH_4)_2SO_4 + 2NaOH = Na_2SO_4 + 2NH_3 + 2H_2O,$$

so that 2NaOH (= 80 gm.) displace $2NH_3$ (= 34 gm.), and the ammonia displaced $= \frac{\cdot 108 \times 34}{80} = \cdot 0459$ gm.

That is, 20 c.c. of the 1 per cent. solution of ammonium sulphate, which contain ·2 gm. of the salt, contain ·0459 gm. of ammonia,

and percentage of ammonia $= \frac{\cdot 0459 \times 100}{\cdot 2} = 22 \cdot 95.$

The pure salt ought to contain $\frac{34 \times 100}{132} = 25 \cdot 76$ per cent. of ammonia.

We can calculate the results in another way.

Since 132 gm. of pure ammonium sulphate require 80 gm. of caustic soda for complete decomposition,

$\therefore$ ·2 gm. pure ammonium sulphate require

$$\frac{\cdot 2 \times 80}{132} = \cdot 121 \text{ gm. NaOH.}$$

But only ·108 gm. were used,

$\therefore$ percentage of pure $(NH_4)_2SO_4$ in the sample taken

$$= \frac{\cdot 108}{\cdot 121} \times 100 = 89 \cdot 3.$$

CHAPTER XVI.

PHOSPHORIC ACID. SILICIC ACID. DIALYSIS. OSMOSIS.

201. **Bones.**—The most rigid part of the framework of our bodies, the skeleton, is made up of bones, and bones when applied in different forms to the land assist in the growth of crops; also the consumption of these crops must supply us with the material for the building of our bones.

Exp. 237.—Take a piece of fresh bone and scrape it free from meat, fat, etc. (a leg bone or rib of the sheep answers well). Crack it into pieces small enough to pass into a test-tube or boiling-tube. (i) Heat one piece on a crucible lid or patty pan; (ii) heat one piece, by itself, in a dry test-tube; (iii) cover a piece with dilute hydrochloric acid, allow it to stand for 24 hours, pour off the acid and evaporate this to dryness; repeat the treatment with hydrochloric acid until the bone is no longer hard, wash, dry, and examine the residue; (iv) heat some of the dry product of (iii), (*a*) on a crucible lid, (*b*) in a test-tube, testing the fumes with red litmus paper. Note the results.

We observe that bone is a hard, brittle substance, which burns when heated in air, and when heated in a test-tube chars, giving off unpleasant-smelling fumes. When treated with dilute hydrochloric acid a white solid is dissolved out and regained on evaporation, while an elastic, translucent model of the bone is left; this model chars in a test-tube and burns in air, leaving a much smaller residue than the original bone (a prolonged digestion with the acid removes nearly the whole of the ash-forming constituents).

The elastic model is found to yield gelatin when boiled with water, and gives off ammonia when heated with quicklime and tested as in Exp. 169, so that it contains nitrogen.

The white solid is most easily investigated after the gelatinous matter has been burnt away, the white or brownish residue which is left being called *bone ash* or *bone earth.*

Bone ash is usually prepared in two stages, the bones being first distilled in absence of air, when a black substance, bone charcoal or *animal charcoal,* is formed, together with *bone oil.*

Exp. 238.—Take a solution of sulphuretted hydrogen in water (Exp. 203), shake some of it with animal charcoal and filter the solution. Test both the original solution and the filtrate with lead acetate.

Take some solution of brown sugar, shake it well with animal charcoal, filter, and note the colour change.

This kind of charcoal possesses in very high degree the property of absorbing gases and substances in solution, and it is largely used in decolourising solutions, such as impure water, sugar solutions, and vegetable extracts; after it is exhausted it is ignited in the air to form bone ash.

202. Bone Ash.

Exp. 239.—Examine a specimen of bone ash. Test its solubility in water (Exp. 208), and test its behaviour with hydrochloric, nitric, and concentrated and dilute sulphuric acids.

We note that bone ash is only very slightly soluble in water, but that it dissolves in hydrochloric and nitric acids. It is partly soluble in dilute sulphuric acid and forms with concentrated sulphuric acid a paste which sets into a cake.

Exp. 240.—Boil 10 c.c. of concentrated sulphuric acid, diluted about 10 times with water, with 20 gm. of bone ash for half an hour or so. Filter, evaporate to dryness, and heat the residue until it no longer fumes. When cold boil the residue with water, test some of it with litmus, add sodium carbonate solution to some more, and evaporate the solution obtained. Note the results.

We observe that the reaction between bone ash and dilute sulphuric acid results in a glassy residue which is acid to litmus and decomposes sodium carbonate, forming a crystalline solid. The acid in solution is called *phosphoric acid,* and in the solid state it is called *glacial phosphoric acid.*

203. Tests for Phosphoric Acid.

Exp. 241.—Boil some of the solution of phosphoric acid with a solution of ammonium molybdate in nitric acid, made by dissolving ammonium molybdate in concentrated ammonia solution and then adding excess of dilute nitric acid (1 in 5). Add ammonia solution to another portion of the phosphoric acid solution until alkaline, then add ammonium chloride and magnesium sulphate solutions. Note the results.

Note.—The solution of magnesium sulphate (or chloride), ammonium chloride, and ammonia is usually kept made up under the name of *magnesia mixture.*

We observe that the ammonium molybdate solution gives a bright yellow precipitate on boiling, and that the magnesia mixture gives a white precipitate. The formation of these precipitates is a *test for phosphoric acid.*

Exp. 242.—Repeat the preceding experiments, using a solution of bone earth in dilute nitric acid. Carefully note what takes place.

We see that ammonium molybdate gives the yellow precipitate formed with salts of phosphoric acid, but that a white precipitate is formed when the solution of the bone ash is neutralised by the ammonia before the addition of magnesia mixture. This white precipitate can be shown to be the original bone ash, so that the second test cannot always be applied.

204. The Composition of Phosphoric Acid. Phosphorus.

Exp. 243.—Place a few grams of phosphoric acid on a crucible lid, warm it carefully, and then make it red hot by the blow pipe. Drop on the red hot liquid some small pieces of aluminium, and watch the result.

The aluminium dissolves and at the same time fumes are given off which burn with a bright yellow flame. The same inflammable gas is formed when phosphoric acid is heated in a closed vessel with carbon, and when this experiment is repeated on a large scale the fumes can be condensed into a yellow liquid which becomes a yellowish solid at about 44° C.; this solid is an element and is called *phosphorus* ; at the same time carbon monoxide is given off, showing that the phosphoric acid must also contain oxygen, and must be derived from an oxide of phosphorus.

205. The Properties of Phosphorus.—We have already examined the burning of phosphorus in air, oxygen, and chlorine.

Exp. 244.—Examine a piece of phosphorus under water.

*(*Demonstration Exp.*) (i) Warm a piece of phosphorus in water in a test-tube; (ii) place a very small piece of phosphorus on a dry piece of blotting-paper in a dark room; (iii) heat a very small piece of phosphorus (or some beetle paste) in a dark room in a flask fitted with a cork and a straight tube about 50 cm. long and half full of water.

We note that phosphorus is a hard, translucent, yellowish solid, insoluble in water, under which it may be cut with a knife; it gives a greenish glow in air or in steam on contact with the air. It is poisonous and is used for killing rats and beetles. The temperature at which it ignites is very low, and it is very readily set on fire by the heat produced by friction or by rubbing with substances containing oxygen such as potassium chlorate or nitrate. It can be and has been largely used in the making of matches, but owing to its poisonous character it is now illegal to use it for that purpose in Great Britain; the sulphide of phosphorus is now generally used instead.

When common yellow phosphorus is kept for about a week at a temperature of 260° C. in absence of oxygen it undergoes a change of colour, becoming deep red and opaque. This substance is purified by digesting it with caustic soda, and after being washed and dried it is found to be a non-inflammable reddish-brown powder; it is called *red* or *amorphous phosphorus* and is not poisonous.

***Exp. 245.**—(*Demonstration Exp.*) Draw off and seal up one end of a piece of narrow glass tube about 25 cm. long. Shake a few grains of red phosphorus down into the closed end and hold the tube horizontally with the closed end in a flame. Note the result.

We see that the red phosphorus forms a cloudy vapour and condenses in the form of yellow globules of the common inflammable phosphorus. Hence, since each form can be converted into the other, solely under the influence of temperature, we may conclude that the red and the yellow are allotropic forms of the same substance, phosphorus.

206. The Oxidation of Phosphorus.—We have already seen that phosphorus burns in air or oxygen, forming white fumes, which dissolve in water to give an acid solution.

Exp. 246.—Burn a small piece of *dry* phosphorus in a small crucible under a *dry* bell jar standing on a *dry* glass plate. Note the change, and scrape together the product. After examining it, drop it into a small quantity of water and test the solution for phosphoric acid (Exp. 241).

We note that phosphorus burns in dry air to form a white solid like snow, which dissolves in water with energy to form phosphoric acid. This white solid is an oxide of phosphorus, called *phosphorus pentoxide,* and the formula P_2O_5 is assigned to it.

207. The Properties of Phosphoric Acid.—Before passing on to consider the formula of phosphoric acid we may compare the phosphoric acid prepared in the last experiment with that prepared by the action of dilute sulphuric acid on bone ash.

Exp. 247.—Take some of each of the solutions prepared as in Exps. 240 and 246, neutralise them carefully with a dilute solution of soda or ammonia, and add nitrate of silver solution to each. To some of each of the solutions add solid sodium acetate, acetic acid, and a solution of white of egg (albumen) in water. Boil some of the solution of phosphorus pentoxide in water, and test again in the same way. Compare the results.

We note that the two acid solutions have different properties, since that prepared direct from bones gives a yellow precipitate with silver nitrate (in neutral solution) and does not affect albumen (in acetic acid solution), while that prepared from phosphorus pentoxide gives a white precipitate with silver nitrate and forms a white curd with albumen. We also note that the acid formed direct from the oxide becomes changed into the other on boiling. The acid prepared direct from the oxide is called *metaphosphoric acid,* and that from bone ash *orthophosphoric acid.*

Orthophosphoric acid is converted into metaphosphoric acid by heat, and the change is accompanied by loss of weight; the only substance which can be identified as being given off is water. Taking this in connection with the last experiment, in which boiling with water converts the meta- into the ortho-acid, we may assume that the two acids differ only in the percentage of water they contain. Thev are found to be represented by the formulae

$$H_2P_2O_6 \text{ or } P_2O_5 + H_2O$$

for the meta-acid, and

$$H_3PO_4 \text{ or } \tfrac{1}{2}(P_2O_5 + 3H_2O)$$

for the ortho-acid.

Orthophosphoric acid contains three hydrogen atoms, and it is important to find out whether they are all replaceable by the metal of a base, and yield three different salts, that is, whether orthophosphoric acid is tribasic (see Art. 175).

Exp. 248.—Place about 10 gm. of commercial phosphoric acid (glacial) in a weighed basin and add to it enough distilled water to make a syrup. Evaporate at 100° C. on a water bath and weigh; heat again at 100° C. and weigh again. When the weight is constant dissolve in such a volume of distilled water as will make a solution containing 9·8 gm. of orthophosphoric acid, H_3PO_4, in 100 c.c. Dissolve also 4 gm. of caustic soda (98 per cent.) in 100 c.c. of distilled water.

Now take three basins and measure into them (i) 10 c.c. of the acid and 10 c.c. of the soda, (ii) 10 c.c. of the acid and 20 c.c. of the soda, and (iii) 10 c.c. of the acid and 30 c.c. of the soda; evaporate all three solutions to the crystallising point and allow them to cool. Dry each batch of crystals on a pad of blotting-paper or a wood pulp block, and test a small quantity of each with litmus, methyl orange, and phenol phthaleïn.

Heat small quantities of each batch to redness on crucible lids, dissolve the products in *cold* water, and add to each (*a*) silver nitrate solution, (*b*) albumen solution and acetic acid. Note the results.

We observe that the three salts are different since they react differently with the indicators, and also, after being heated, with neutral silver nitrate and acidified albumen, so that we have been able to prepare three different phosphates of soda.

Orthophosphoric acid thus forms three different salts with caustic soda, and we confirm the fact that it contains three hydrogen atoms replaceable by sodium. The formula of the acid is confirmed as H_3PO_4, in which case the three sodium salts are represented by the formulae—

Na_3PO_4,	called normal sodium orthophosphate or trisodium phosphate.
Na_2HPO_4,	called disodium hydrogen orthophosphate or common sodium phosphate.
NaH_2PO_4,	called sodium dihydrogen orthophosphate or acid sodium phosphate.

Note.—The salt from (iii) is alkaline to all indicators, and after heating yields a yellow precipitate with silver nitrate and no precipitate with acidified albumen. The salt from (ii) is alkaline to litmus and methyl orange, but neutral to phenol phthalëin. After heating it yields a white precipitate (generally yellowish) with silver nitrate and no precipitate with albumen. The salt from (i) is acid to litmus and phenol phthalëin, but neutral to methyl orange, and after heating yields a white precipitate with silver nitrate, and a white precipitate with albumen.

208. The Soil. Silicic Acid. Silica.—We have already seen that plants leave an ash when burnt; the ash varies in amount, but in the case of the cereals it amounts to about 5 per cent. of the weight of the dry plant. The substances which go to form the ash must be derived from the soil.

Exp. 249.—Heat 2 or 3 gm. of soil in a dry test-tube and test any vapour for water and ammonia. Also heat an equal quantity of soil to redness on an iron or porcelain dish.

We first notice that water is given off and a cultivated soil generally blackens or chars. The charred soil usually turns reddish or brownish after being heated to redness in the open air. The unburned residue, except in the case of Fen soils, forms from 85 to 95 per cent. by weight of the original soil.

Exp. 250.—Place 2 or 3 gm. of the heated soil in a boiling tube or basin, add concentrated hydrochloric acid and boil. Note what takes place. Dilute and filter the solution and test by (i) ammonia, (ii) boiling with nitric acid and ammonium molybdate, (iii) barium chloride and hydrochloric acid. Boil a small quantity of the soil with dilute nitric acid, filter, and add silver nitrate solution.

We note generally a fizzing on the addition of the acid, the formation of a coloured solution, and the presence of a large residue which remains a dirty white colour after washing.

The coloured solution generally gives (i) a bulky precipitate with ammonia, indicating the formation of insoluble metallic hydroxides, (ii) a varying quantity of yellow precipitate with ammonium molybdate and nitric acid, indicating the presence of phosphoric acid, (iii) a cloudiness with barium chloride and hydrochloric acid, indicating the presence of sulphuric acid, and (iv) a cloudiness with silver nitrate and nitric acid, indicating the presence of hydrochloric acid. (ii), (iii), and (iv) all vary with the soil tested.

The residue does not dissolve in acids, so it may itself be an acid or a neutral body.

Exp. 251.—Boil some of the residue with caustic soda solution and acidify the solution when cool. Place in a nickel crucible or iron spoon about 2 gm. of the residue with 5 times its weight of solid caustic soda, or better, dried sodium carbonate to which half its weight of potassium carbonate has been added to make it melt more easily. Heat for 10 minutes in the flame of a blowpipe or blast burner. Allow to cool, place the solid in water and boil till the lumps break up. Filter and add excess of hydrochloric acid to the solution. Filter off any gelatinous precipitate, dry it, and heat it to redness in a crucible. Evaporate the filtrate to dryness and heat to redness.

We observe (i) that the soil almost entirely dissolves in the melted carbonates, and that the product mostly dissolves in water leaving a small residue; this residue is found to contain carbonates of metals; (ii) that the solution when acidified deposits a thick gelatinous precipitate which, on being heated to redness, becomes a white powder; (iii) that the solution filtered from the precipitate when evaporated to dryness still yields a similar white powder which must have been in solution.

After heating, the white solid is insoluble in water and can be weighed. An examination of different soils and rocks shows that they contain varying amounts of this solid, from about 55 to 60 per cent. in clay soils to about 80 to 90 per cent. in sandy soils and nearly 100 per cent. in flint and quartz, so that it is an essential constituent of soils.

It can be shown that this white solid, which is called *silica*, is a dioxide of an element *silicon* of atomic weight = 28, and is represented by the formula SiO_2. The element silicon resembles carbon in its properties, and may be prepared in a hard state; its oxide resembles carbon dioxide in being a weak acid oxide. The gelatinous precipitate contains water, turns litmus slightly red, dissolves in caustic soda, and may be approximately represented by the formula H_2SiO_3; it is called *silicic acid* and resembles carbonic acid, H_2CO_3, except that its salts are much greater in number and complexity, and build up most of the rocks and soils of the crust of the earth.

The salts of silicic acid are called *silicates*; in addition to the natural silicates, many others are used commercially and will be considered later.

Sodium silicate, prepared by fusing fine white sand with 1½ times its weight of sodium carbonate, dissolves in water forming a syrupy solution called *water-glass*, used for preserving eggs. The solution contains sodium silicate represented by the formula Na_2SiO_3.

209. Dialysis.—In Exp. 251 we noted that the gelatinous silicic acid can be separated from the solution by filter paper, but that some of the acid passed through the filter paper in solution and was obtained when the liquid was evaporated and heated to redness. An explanation would appear to be that the silicic acid molecules are of different sizes; some of them can pass through the small holes in filter paper, which have an approximate diameter of $\frac{1}{1000}$ mm. (·001 mm.), while others cannot, and must, therefore, have a larger diameter than ·001 mm.

This phenomenon is not uncommon, and may be seen when sulphuric acid is precipitated with barium chloride, and phosphoric acid with magnesia mixture, but in these cases the particles of the precipitate seem to grow larger on standing, and in a comparatively short time they grow too large to pass through the holes in the paper.

We know further that while the substances making up plant food have to pass into the plant through the thin skin or membrane surrounding the root hairs, only a comparatively small quantity of silicic acid appears to be able to get through, except in the case of the cereals, though it forms such a large proportion of the soil.

Exp. 252.—Cut some circles of bladder, parchment, or parchment paper, fold them into cones like filter papers, and pin or clip them into shape as near the edge as possible. Pour into these cones strong solutions of nitre, potassium dichromate, white of egg (egg albumen) and litmus, either separately or mixed, but not reaching the holes made by the pins: examine at intervals. Now rest the cones in beakers nearly full of distilled water (Fig. 82), and watch the effect. In a few minutes test the water in the beakers for nitrates, note its colour, and test by boiling for the white of egg.

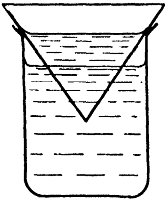

Fig. 82.

We note first that the cones when filled with the solution only get wet on the outside very slowly, so that the parchment paper must have much smaller holes than filter paper; they are estimated to be $\frac{1}{1000000}$ mm. in diameter. We next observe that when the cones are allowed to dip into water the water below the potassium dichromate shows yellow streaks, while no colour is observed in the case of litmus, also that streaks are visible running down from the point of the nitre cone; the water shows that nitrate has passed through, while very little egg albumen has passed through.

It appears, therefore, that some substances in solution are able to pass through parchment paper into a liquid in contact with the other side of the paper, while other substances cannot pass. The phenomenon resembles the diffusion of gases from one place to another, and the passage of substances in solution through parchment paper or membranes is called *dialysis*. Now we know that the diameter of the gaseous molecule is about $\frac{1}{100000000}$ mm. which is only $\frac{1}{100}$ of the diameter of the holes in parchment paper, so that by analogy with filtration by filter paper we may assume that parchment paper separates molecules or particles of a greater diameter than $\frac{1}{1000000}$ mm., which will not pass through it, from the smaller molecules, which will dialyse through.

Exp. 253.—To some water glass solution add dilute hydrochloric acid until the solution is acid. Take a piece of parchment paper tube, make a loop of it and pass a piece of glass rod through holes at the open ends. Half fill the tube with the acid solution and suspend in a jar or beaker of distilled water with the glass rod across the top (Fig. 83). After standing test some of the water with silver nitrate solution, change the water, and go on until there is no hydrochloric acid to be found. Now test the contents of the tube and of the jar by adding ammonium carbonate, by evaporation, and by silver nitrate.

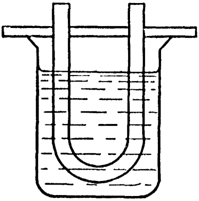

Fig. 83.

It will be seen that the hydrochloric acid and common salt have all dialysed through the paper and been thrown away, while the contents of the tube but not of the jar gelatinise by the addition of the ammonium salt. The gelatinous precipitate is silicic acid, and it appears that its particles, though in solution, are too large to pass through the holes in the paper.

When this phenomenon was first discovered by Thomas Graham it was thought that only gelatinous substances refused to dialyse, while all crystalline substances would dialyse, so that the former were called *colloids* and the latter *crystalloids*. This has now been found not to be strictly true. But the *colloids*, or substances with large particles of the order of $\frac{1}{1000000}$ mm. diameter or more, are of extraordinary importance in the building up of living matter and the fixing of its properties. Silicic acid in solution is a colloid.

210. Osmosis.—If the water in the jar in Exp. 253 is not changed it can be shown by standard silver nitrate solution that the percentage of chlorides in the jar increases until it is exactly equal to the concentration of the chlorides in the tube, so that just as much must be passing into the jar from the tube as is passing back into the tube from the jar; the silicic acid, however, cannot pass through.

Exp. 254.—Take a piece of gelatin and lay it in water for an hour. Take a fresh egg and dip it in dilute acetic acid or vinegar until the shell is quite soft; next place the egg in water for 24 hours. Then put the gelatin in spirit and the egg in strong salt brine.

We note that in water the gelatin swells and the egg becomes plump and round, while in the alcohol and the brine the gelatin contracts again and the egg becomes smaller and shrivels. It seems, then, that when the colloid cannot get to the water the water diffuses or dialyses into the colloid, while when the water in the colloid can get out into a more concentrated solution it does so, leaving the colloid behind.

This phenomenon is called *osmosis,* and the process of osmosis enables plant and animal cells to take up water for their life and growth. If the cell contents are less concentrated as regards any dialysable salt or substance than the surrounding soil water or other solution, this will dialyse through into the cell until the concentration is the same inside and out; each substance generally is independent of any others.

Similarly, if the cell contents are more concentrated than the solution outside, water will pass in by osmosis and the excess of the dissolved crystalloid will pass out until equilibrium is reached. It is further noted that the passage of water into a closed cell more quickly than it can get out results in the production of increased pressure within the cell and vice versa; this pressure resembles that produced in the diffusion of gases, and is termed *osmotic pressure.*

CHAPTER XVII.

CHALK : LIME : CALCIUM COMPOUNDS.

211. **Calcium Carbonate.**—We have already examined chalk, marble, quicklime, and slaked lime, and have come to the conclusion that they are all compounds of the metal *calcium* (Art. 149), quicklime being its oxide, CaO, slaked lime its hydroxide, $Ca(OH)_2$, and chalk and marble its carbonate, $CaCO_3$.

Calcium carbonate is perhaps the most important natural compound of calcium, and in addition to its occurrence as chalk and marble, it is also largely found as limestone, coral, and oyster shells.

Calcium carbonate neutralises most acids and is a very important constituent of fertile soils, in which it not only neutralises acids which cause sourness, but also acts as a source of plant food. It is easy to prepare other calcium salts from chalk by the action of acids, but perhaps its most important use agriculturally is for the preparation of quicklime.

212. **Quicklime.**—Quicklime is manufactured from all forms of calcium carbonate, but most generally from chalk and limestone, by the process of *lime-burning*. In this process the chalk is roasted in a slow draught of air in vertical conical kilns, with the narrow end downwards. The fire is started and then lumps of chalk mixed with small coal, cinders, or wood are gradually added. As the carbon dioxide is given off (Exp. 49) it is carried away in the stream of air, and as the quicklime gradually reaches the bottom it is raked out as required, fresh chalk and fuel being added at the top.

Owing to the method of preparation a certain amount of the carbonate may remain undecomposed and lower the value of the product, but good agricultural lime should not contain more than 15 per cent. of chalk. Any impurities in the original carbonate used for burning will remain in the quicklime and affect its properties. Thus 5 to 15 per cent. of clay will cause the quicklime to slake slowly and prevent it from forming the fine powder necessary for spreading on the land to the best advantage. The effect of the clay is to cause the lime to become cement.

213. The Action of Air on Quicklime.

Exp. 255.—Place some lumps of quicklime in the air. Examine some quicklime which has been exposed to the air for some time. Test it by water, litmus, and acids.

We note that quicklime when exposed to the air for a long time crumbles to a powder which does not become hot when water is poured over it : it is said to be *air-slaked.*

Exp. 256.—Heat some air-slaked lime in a dry test-tube, and test any products.

We note that air-slaked lime has absorbed water from the air, and has become converted into hydroxide and some carbonate ; this confirms our use of quicklime as a drying agent.

Slaked lime is largely used in the making of mortar and cements, as it gradually becomes hard, or *sets.*

Exp. 257.—Take a piece of old mortar, or slaked lime which has been exposed to the air for a long time, and test it with litmus and with hydrochloric acid.

We observe that the slaked lime has gradually become converted again, by the absorption of carbon dioxide from the air, into the carbonate from which it was originally made. The carbonate formed in this way is hard and durable.

214. The Estimation of Quicklime.—Quicklime, when pure and free from carbonate, can be readily estimated by means of standard acid added until the solution is neutral to methyl orange, but as the solid is only slowly dissolved by water it is better to add a measured excess of the acid and determine the excess by standard alkali.

Exp. 258.—Pipette out 50 c.c. of freshly prepared lime water, add a few drops of methyl orange and neutralise with standard 1 per cent. hydrochloric acid.

The results obtained can be calculated in terms of grams of CaO per litre, using the neutralisation equation

$$CaO + 2HCl = H_2O + CaCl_2.$$

The second method enables us to determine the percentage of total calcium oxide in a calcium carbonate or mixture of calcium carbonate and calcium oxide ; but for an accurate result, as in the case of all naturally occurring solids, it is necessary to powder the solid very carefully before weighing it.

Exp. 259.—Weigh out accurately on a watch glass about 1 gm. of a very carefully powdered specimen of commercial lime, limestone, or air-slaked lime ; wash it by means of a jet of water from a wash bottle into a 250 c.c. flask ; add 200 c.c. of 1 per cent. HCl solution and make up to the mark. When all action appears to have stopped, pipette off 50 c.c. into a beaker and neutralise with 1 per cent. NaOH, using methyl orange as an indicator.

In an experiment using 1·00 gm. of the sample, the average number of c.c. of 1 per cent. NaOH solution required was found to be 24·1. The result may be calculated thus :—

24·1 c.c. 1 per cent. NaOH solution contain ·241 gm. NaOH.

From the equation

$$NaOH + HCl = H_2O + NaCl,$$

$$\cdot241 \text{ gm. NaOH neutralise } \frac{\cdot241 \times 36\cdot5}{40} = \cdot220 \text{ gm. HCl}$$

$$= \text{excess of HCl in 50 c.c. solution.}$$

$$\therefore \text{ excess of HCl in 250 c.c. solution} = \frac{\cdot220 \times 250}{50} = 1\cdot10 \text{ gm.}$$

Since 200 c.c. of 1 per cent. HCl solution contain 2 gm. HCl, the difference = 2·00 − 1·10 = ·90 gm. represents the HCl neutralised by 1 gm. of the sample taken.

From the equation

$$CaO + 2HCl = H_2O + CaCl_2,$$

56 gm. (= Ca + O) of lime are required to neutralise 73 gm. (= 2HCl) of hydrochloric acid.

∴ lime contained in 1 gm. of the sample $= \frac{\cdot 90 \times 56}{73} = \cdot 694$ gm.

and the sample contains 69·4 per cent. of CaO.

Now samples of quicklime nearly always contain some undecomposed calcium carbonate which will itself neutralise acids. By using phenol phthalëin as an indicator and boiling the weighed lime and water while running in a standard solution of HCl until the colour is just discharged only the CaO is neutralised, and the above equation (Exp. 258) can be used. But it has been found that quicklime combines with phenol or carbolic acid, and that the compound is readily soluble in water, while calcium carbonate is unattacked and remains insoluble. The phenol compound neutralises the commoner acids just as lime does, and methyl orange is a suitable indicator. This method is very convenient.

Exp. 260.—Weigh out on a watch glass about 2 gm. of the carefully powdered and mixed quicklime and wash it into a 250 c.c. flask; add about 100 c.c. of a 5 per cent. solution of pure phenol (or add 5 gm. of the crystals and 100 c.c. water); shake for a few minutes from time to time for half an hour, and make up to the mark. Filter off about half the solution and pipette 50 c.c. into a beaker; add a few drops of methyl orange, and neutralise with standard HCl solution.

In one experiment 1·85 gm. of lime were weighed and made up as above. 50 c.c. of the filtrate were found to require an average of 41·0 c.c. of 1 per cent. HCl solution.

That is, 250 c.c. of solution required for neutralisation

$$\frac{\cdot 41 \times 250}{50} = 2{\cdot}05 \text{ gm. HCl.}$$

But from the equation

$$CaO + 2HCl = H_2O + CaCl_2,$$

73 gm. HCl neutralise 56 gm. CaO.

∴ 250 c.c. of the solution (= 1·85 gm. sample) contain

$$\frac{2{\cdot}05 \times 56}{73} = 1{\cdot}57 \text{ gm. CaO,}$$

and the percentage of CaO in the sample taken

$$= \frac{1{\cdot}57 \times 100}{1{\cdot}85} = 84{\cdot}9.$$

215. Tests for Calcium.—Calcium is so generally distributed in fertile soils that it is necessary to find tests for it.

Exp. 261.—Heat a piece of chalk and a piece of quicklime in the Bunsen flame. Moisten a corner of each piece with hydrochloric acid, and repeat the experiment.

We note that though neither chalk nor lime colours the flame much, yet when moistened with hydrochloric acid, each colours it orange red.

Exp. 262.—Dissolve some calcium chloride in water and add to the solution (i) ammonia and ammonium carbonate, (ii) ammonia and ammonium oxalate.

We note that solutions of calcium compounds give white precipitates with both reagents, and these are used as tests for the presence of calcium in solution.

216. Calcium Chloride.

Exp. 263.—Take about 20 c.c. of hydrochloric acid in an evaporating basin; add chalk or marble until some remains undissolved. Filter, if necessary, and evaporate till crystals begin to form. Dry the crystals with blotting-paper as quickly as possible. Heat some of the crystals in a test-tube. Test both the crystals and the solid obtained on heating, by litmus and also by silver nitrate and nitric acid.

We observe that chalk dissolves in hydrochloric acid to form a crystalline neutral solid, which on being heated gives off water, leaving a dry solid which is a *chloride of calcium*.

An equation which represents the reaction is

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$$

If the crystals are dried rapidly, the water of crystallisation may be estimated as in Exp. 213. The formula for the crystals is found to be $CaCl_2, 6H_2O$, taking 40 as the atomic weight of calcium. Calcium chloride when free from water or *anhydrous* readily absorbs water from gases as we have already seen, and it is used as a drying agent.

Exp. 264.—To a solution of calcium chloride add caustic soda. Filter off the precipitate and wash well with water. Test it for calcium, for chlorides, and by litmus.

Caustic soda thus gives with calcium chloride a white precipitate, which contains calcium and is alkaline, but is free from chlorides. This precipitate is the hydroxide of calcium, slaked lime. An equation which represents the reaction is

$$CaCl_2\,Aq + 2NaOH\,Aq = Ca(OH)_2 + 2NaCl\,Aq.$$

It cannot escape notice that a single atom of calcium combines with the same amount of carbon dioxide or of chlorine as two atoms of sodium. This property is termed the *acidity* of the base of the metal, so that if sodium forms a *monacid base*, calcium forms a *diacid base*. We also notice that the acidity of the base is the same as the number of groups of one oxygen atom and one hydrogen atom, i.e. *hydroxyl* groups, in the base.

217. The Properties of Calcium Sulphate.

Exp. 265.—Examine specimens of gypsum or selenite, and boil them up with water. Boil also specimens of soil with water. Filter all the solutions and test them for calcium and for a sulphate.

Exp. 266.—Make a saturated solution of calcium sulphate. Place 20 c.c. in an evaporating basin, and evaporate to dryness.

We note that gypsum and ordinary soil contain calcium sulphate, and that it is slightly soluble in water ; it is about as soluble as slaked lime, viz., 1·8 gm. in 1 litre. It is, however, much more soluble than calcium carbonate, so that it is decomposed and precipitated by sodium carbonate, and we may write an equation to represent that reaction, in which calcium sulphate is represented by the formula $CaSO_4$.

$$CaSO_4\,Aq + Na_2CO_3\,Aq = CaCO_3 + Na_2SO_4\,Aq.$$

Exp. 267.—Heat some gypsum in a hard glass tube, and note any change.

Exp. 268.—Repeat Exp. 213, using gypsum, and find the percentage loss. Calculate the number of molecules of water, taking Ca as 40.

We find that gypsum gives off water when heated, and that it is represented by the formula $CaSO_4,2H_2O$. If the heating is stopped just before the whole of the water is expelled, then it can combine again with water when they are mixed. In this state the gypsum is called *plaster of Paris.*

218. The Action of Carbon Dioxide on Lime-water.—We have used lime-water as a test for carbon dioxide, and have partly investigated the reaction between them. (Exp. 48.)

Exp. 269.—Shake up chalk with boiled distilled water, and evaporate 20 c.c. of the liquid to dryness.

Exp. 270.—Pass carbon dioxide through freshly prepared lime-water until it is very milky. Boil and filter the liquid. Test the precipitate left on the filter paper for calcium and for a carbonate.

Slaked lime is much more soluble in water than chalk, which is hardly soluble at all, and the precipitate obtained when carbon dioxide is passed through lime-water consists of calcium carbonate. Hence carbon dioxide when passed through lime-water combines with the lime, forming the carbonate of calcium, which is less soluble and is precipitated. The change may be represented by an equation, thus :—

$$Ca(OH)_2\ Aq + CO_2 = CaCO_3 + H_2O\ Aq.$$

Exp. 271.—Dilute some freshly prepared lime-water with about an equal volume of distilled water. Now pass carbon dioxide through it for some time. Test the solution for calcium and carbonic acid, and by litmus.

We see that when excess of carbon dioxide is passed through lime-water, the chalk which is first precipitated dissolves in the form of a carbonate which is slightly acid to litmus.

Exp. 272.—Boil the solution just prepared by passing excess of carbon dioxide through diluted lime-water. Test the precipitate, the solution, and the gases given off for calcium and for carbon dioxide.

We note that the soluble carbonate of calcium is destroyed by boiling, forming the insoluble carbonate and giving off carbon dioxide. An explanation is found in the assumption that carbon dioxide solution in water contains carbonic acid, and that calcium forms a soluble bicarbonate which exists only in solution and is decomposed by boiling. Equations may be made to represent this change, where $CaH_2(CO_3)_2$ represents calcium bicarbonate; compare Art. 186.

$$CaCO_3 + H_2CO_3, Aq = CaH_2(CO_3)_2, Aq,$$

$$CaH_2(CO_3)_2, Aq = CaCO_3 + CO_2 + H_2O, Aq.$$

219. Hardness of Water.—The formation of a precipitate on boiling reminds us of the fact that hard waters deposit a crust or fur on the kettle or vessel in which they are boiled.

Exp. 273.—Boil some hard spring or river water or soil water in a flask or beaker. When it has been boiling a few minutes, pour the water off, and test the solid residue left in the flask for calcium and for carbonic acid.

It appears that spring or river water and soil water may contain chalk dissolved in carbonic acid in the form of calcium bicarbonate, and that the chalk is precipitated on boiling, as in the preceding case. Such water is called *hard water*, because it is difficult to obtain a lather by means of soap when using the water, and so the water feels hard to the touch.

Exp. 274.—Dissolve 10 gm. of Castile soap in shavings or of sodium oleate in distilled water, and make up to a litre. The solution keeps better if about ¼ litre of methylated spirit is added before making up to the litre. Into a stoppered bottle measure 50 c.c. of hard water, and run in the soap solution from a burette, shaking the bottle well after each addition until the lather does not break or allow the water to show through the froth in five minutes.

Repeat the experiment with 50 c.c. of hard water which has been boiled, and with 50 c.c. of distilled water.

We observe (i) that the hard water takes many c.c. of soap solution to make a permanent lather, while the soft water only takes a few, say 2 or 3 c.c., and (ii) that the hardness produced by chalk in the form of calcium bicarbonate is almost entirely destroyed by boiling. Such hardness is called *temporary hardness*.

Exp. 275.—Shake up some calcium sulphate with water. Test 50 c.c. with the soap solution, as in the last experiment. Boil the calcium sulphate solution and test 50 c.c. of the boiled solution with soap.

We find that the water containing calcium sulphate in solution is hard, and that the hardness is not lessened by boiling. Such hardness is called *permanent hardness.*

Exp. 276.—To the solution of calcium sulphate add washing soda, and boil. Find the number of c.c. of soap solution required to produce a permanent lather with 50 c.c. of the filtrate.

We infer that we can reduce the hardness of permanently hard water by boiling with sodium carbonate, which precipitates calcium carbonate.

The calcium bicarbonate contained in spring, river, and soil water is derived from calcium carbonate existing in the soil. Rain water usually contains carbon dioxide, and it dissolves more of this gas from the soil on which it falls ; the carbonic acid thus formed then dissolves chalk, etc., in the form of calcium bicarbonate, which is carried away and used by plants in solution.

220. Phosphates of Calcium.

Exp. 277.—Take 30 gm. of bone ash and pour on it 10 c.c. of concentrated sulphuric acid diluted with an equal volume of water ; allow the mixture to stand until set ; add water, shake up, and filter. Evaporate one half of the solution to dryness, and to the other half carefully add chalk until no further fizzing is noticed, then filter, wash the solid, and dry it.

Test both solids for lime and for phosphoric acid. Find the solubilities of the salts as in Exp. 208, and compare with the solubility of bone ash (Exp. 239). Compare also the reactions with litmus, methyl orange, and phenol phthalëin.

We observe that we have been able to prepare two phosphates of lime, which differ from bone ash in solubility and reactions.

These two phosphates are called respectively *superphosphate,* and *reduced* or *reverted calcium phosphate,* and together with bone ash they correspond with the three sodium phosphates (Art. 207). The following formulae are assigned to them :—

$Ca_3(PO_4)_2$.	Bone ash or tricalcium orthophosphate.
$Ca_2H_2(PO_4)_2$ or $CaH(PO_4)$.	Reduced or reverted calcium phosphate or calcium hydrogen orthophosphate.

$CaH_4(PO_4)_2$.	Calcium superphosphate or calcium tetrahydrogen orthophosphate.

The calcium orthophosphates are sometimes expressed by rather different formulae as compounds derived from phosphoric oxide and quicklime, thus :—

$3H_2O, P_2O_5$.	Phosphoric acid.
$2H_2O, CaO, P_2O_5$.	Calcium superphosphate.
$H_2O, 2CaO, P_2O_5$.	Reduced phosphate.
$3CaO, P_2O_5$.	Bone ash.

These formulae make it easier to understand the changes of one phosphate into another.

Calcium tetrahydrogen orthophosphate is used as a manure on a large scale under the name of *superphosphate of lime.* Now from the last experiment we noticed that the action of chalk on this superphosphate converts it into reduced phosphate. This change takes place in the soil shortly after the application when superphosphate is used as a manure. Hence there is a tendency in the case of a heavy superphosphate dressing to remove an excessive amount of chalk from soils which are poor in that constituent (*e.g.* peat) and to make them acid. However, the great initial solubility tends to spread the more soluble phosphates throughout the surface soil so that they are ready for use by the young plant, and much heavier dressings of less soluble or less acid phosphates are required to produce the same immediate effect as a small dressing of the more soluble superphosphates.

Exp. 278.—Boil a mixture of bone ash and quicklime with water. Filter and test the solution by litmus and by ammonium molybdate.

We note that bone ash is slightly soluble in lime-water, making an alkaline solution. This is due to the formation of a compound containing an excess of lime, and represented by the formula $4CaO, P_2O_5$.

Another phosphatic manure in extensive use is called *basic* *slag.* It is prepared in the purification of iron from phosphorus by the oxidation of the phosphorus contained in the molten metal by blasts of hot air ; the phosphoric oxide is absorbed by quicklime, which is mixed with the fire-clay lining of the vessels in which the iron is heated, and the linings are ground up and sold as basic slag.

Exp. 279.—Test some finely ground basic slag as in the last experiment ; pass some carbon dioxide through the solution.

We note that basic slag is alkaline and contains a phosphate of calcium and quicklime. It is conveniently represented by the formula $4CaO, P_2O_5$ as above.

CHAPTER XVIII.

MAGNESIUM COMPOUNDS.

221. Magnesium.—We have already (Art. 63) made use of the metal magnesium in determining the composition of water, and have found (Art. 148) that it forms a definite oxide, magnesia, represented by the formula MgO, and a hydroxide represented by the formula $Mg(OH)_2$. The metal itself is greyish white and soft enough to be rolled into ribbon; its atomic weight is taken as 24.

The compounds of magnesium resemble generally those of calcium except that they differ in solubility and taste. Magnesium appears to be essential to plant life, but in such small quantities that it can be supplied by most soils; we therefore require a test for magnesium compounds.

222. Tests for Magnesium Compounds.

Exp. 280.—Take a solution of magnesium in dilute hydrochloric acid and add ammonium carbonate solution. A precipitate is formed similar to the calcium carbonate formed in Exp. 262. Now add an equal volume of a strong solution of ammonium chloride: the precipitate dissolves.

A calcium carbonate precipitate does not dissolve in ammonium chloride solution, so that we can distinguish between the two carbonates and precipitate all the calcium compound by ammonium carbonate in presence of ammonium chloride.

Exp. 281.—Add to solutions of calcium and magnesium chlorides a solution of ammonia and sodium phosphate; both solutions give precipitates of insoluble phosphates. Now add to each an equal volume of a saturated solution of ammonium citrate.

The calcium phosphate dissolves, while the magnesium phosphate does not, so that we can test for magnesium *either* by means of sodium phosphate, after removing calcium by ammonium carbonate and ammonium chloride, *or* in presence of calcium compounds by adding ammonium citrate before adding the ammonia and sodium phosphate.

The precipitate formed by magnesium compounds with sodium phosphate and ammonia is represented by the formula $Mg(NH_4)PO_4, 6H_2O$, and is called *magnesium ammonium phosphate.* It is sufficiently insoluble in water to be used in determining the percentage of magnesia or phosphoric acid in manures, and can either be weighed after drying or be decomposed by being made red hot in a crucible, when it is weighed as a phosphate represented by the formula $Mg_2P_2O_7$. The action of heat is represented by the equation

$$2Mg(NH_4)PO_4, 6H_2O = Mg_2P_2O_7 + 2NH_3 + 13H_2O.$$

223. Magnesium Carbonate.—Magnesium compounds are more conveniently obtained from natural sources than calcium compounds. The most plentiful supply is contained in the carbonates, *magnesite,* $MgCO_3$, and *dolomite* or *magnesian limestone,* which is found in many places, and is a carbonate of calcium and magnesium in which the two metals are interchangeable; the formula $(Mg, Ca)CO_3$ is generally assigned to this substance. Magnesium carbonate on being heated to redness gives off carbon dioxide and becomes magnesia, MgO. It also dissolves in carbonic acid forming magnesium bicarbonate, $MgH_2(CO_3)_2$, which makes water temporarily hard.

224. Magnesia, MgO.–The oxide magnesia is usually prepared from magnesite by heating, in which case it is a dense white powder very slightly soluble in water and making the solution alkaline from the presence of the hydroxide, $Mg(OH)_2$.

225. Magnesium Chloride.—Magnesium chloride is prepared from magnesite or magnesia by dissolving in hydrochloric acid and evaporating until it crystallises out in the form of colourless crystals, having the formula $MgCl_2, 6H_2O$.

Exp. 282.—Test sea water or sea salt and kainit for magnesium compounds.

We note that sea water, sea salt, and kainit all contain large quantities of magnesium compounds, which impart a characteristic bitter taste. Magnesium chloride resembles calcium chloride in being very deliquescent, so that sea salt is apt to get wet in damp climates. Common salt contains traces of magnesium chloride, and the tendency to deliquesce may be neutralised by the addition of a salt which gives up water in air ; *e.g.* sodium sulphate or sodium phosphate.

Exp. 283.—Heat a few crystals of magnesium chloride in a test-tube and test the fumes given off for hydrochloric acid.

We note that magnesium chloride when heated gives off first water and then hydrochloric acid gas.

226. Other Magnesium Compounds.

Exp. 284.—Test a solution of Epsom salts for magnesium compounds and for sulphates.

Epsom salts are found to be a sulphate of magnesia represented by the formula $MgSO_4, 7H_2O$. It will be noted that there is a characteristic difference between this salt and calcium sulphate, since the former is soluble and the latter only slightly soluble in water.

Other magnesium compounds are found as silicates in meerschaum, talc or mica, and a large number of rocks.

CHAPTER XIX.

IRON AND ALUMINIUM.

227. Iron.—We have already examined some of the physical properties of iron, and have classified it as a metal.

Exp. 285.—Examine the reactions of iron with strong and weak hydrochloric, nitric, and sulphuric acids, both when hot and in the cold. Test any gases given off, and evaporate the solutions formed.

We note that iron dissolves in hydrochloric, nitric, and dilute sulphuric acids in the cold, and in strong sulphuric acid when hot.

228. The Sulphates of Iron.

Exp. 286.—Into a flask pour about 100 c.c. of dilute sulphuric acid, and add iron filings. Allow the reaction to proceed, warming the flask when it slackens and keeping the iron in excess. When all the action has stopped, filter the solution while hot, and allow one half to crystallise by itself; to the other half add some methylated spirit and then allow it to crystallise. Pour off the liquor from both lots of crystals, and dry them on blotting-paper. Allow some of the crystals to stand in the air.

We note that green crystals separate out as the solutions cool: these are called crystals of *green vitriol.*

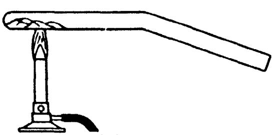

Fig. 84.

Exp. 287.—Into a hard glass test-tube bent in the middle at about 120° place about 5 gm. of the green crystals. Support the tube with the closed limb horizontal (Fig. 84) and heat the crystals. Note the various changes and collect and examine the products.

We observe that water and fumes of sulphuric acid are given off, and that a red powder is left behind; this red powder is called *rouge*. The heating of green vitriol crystals is a very old method of preparing strong fuming sulphuric acid or Nordhausen sulphuric acid, represented approximately by the formula, $2H_2SO_4, SO_3$.

Exp. 288.—Warm the red residue with four or five drops of strong sulphuric acid, evaporate to dryness; allow it to cool and then add water.

We observe that a brown solution is obtained when the red residue is dissolved in sulphuric acid, while when the metal was dissolved we noted that green crystals were formed.

To determine the relationship between these two substances, the green crystals and the brown solution, we must be able to identify them.

Exp. 289.—Dissolve some of the green crystals in water, and add solutions of (i) soda, (ii) potassium ferrocyanide, (iii) potassium ferricyanide, (iv) potassium sulphocyanide, (v) barium chloride. Repeat the tests with the brown solution prepared in the last experiment.

We observe that the solution of the green crystals gives a greenish precipitate with soda, a light blue precipitate with the ferrocyanide, a dark blue precipitate with the ferricyanide, and only a pink colour with the sulphocyanide, while the brown solution gives a brown precipitate with soda, a dark blue (Prussian blue) precipitate with the ferrocyanide, a brownish solution without any precipitate with the ferricyanide, and a deep blood-red solution with the sulphocyanide.

From reaction (v) we infer that both substances are sulphates, and since iron has not volatilised they contain the iron from which they were made, but the two are evidently different.

Now we have already (Exp. 141) examined the reaction between ferrous sulphate and nitric acid which results in the formation of nitric oxide.

Exp. 290.—Put some of the green sulphate crystals into an evaporating basin, and add dilute sulphuric acid and a few drops of nitric acid. Evaporate to dryness and test the residue by dissolving it in water and applying the reagents used in the last experiment.

We find that the brown sulphate of iron can be prepared by the action of nitric acid on the green sulphate solution, nitric oxide being given off. We have already decided that nitric acid is an oxidising agent, and the formation of nitric oxide shows that reduction of the nitric acid has taken place. Oxygen must have been used up in the reaction and not given off in a free state, or nitrous fumes would have appeared instead of nitric oxide, even in absence of air. It is probable, therefore, that the brown sulphate is the green sulphate oxidised. If this is the case, we ought to be able to pass from the green to the brown sulphate by oxidation, and from the brown to the green by reduction.

Exp. 291.—Examine the two sets of crystals of the green sulphate which were allowed to stand in the air. Allow some of the green sulphate solution to stand in air or oxygen. To portions of the green sulphate solution add dilute sulphuric acid and (i) potassium permanganate, (ii) potassium dichromate. Also warm portions of the brown sulphate solution with (i) sulphurous acid, and (ii) sulphuretted hydrogen, and boil a portion with (iii) iron. Test in each case by potassium ferricyanide and potassium sulphocyanide.

We observe that we can pass from the green to the brown sulphate by oxidation, and from the brown to the green by reduction. We indicate this connection between the green and brown sulphates in the usual way by the terminations *-ous* and *-ic*. Thus the green sulphate, which contains relatively less oxygen, is called *ferrous sulphate*, and the brown sulphate, which contains relatively more oxygen, is called *ferric sulphate.*

We also note that the green crystals from the water solution readily oxidise in the air, while those from the weak methylated spirit change very slowly : the fact need not be explained here, but it enables us to prepare and keep the pure sulphate.

Before fixing formulae to represent these two sulphates of iron, we must examine the basic oxides and bases which correspond with these salts.

229. The Oxides of Iron.

Exp. 292.—Take some ferrous sulphate crystals, wash them with water, and then dissolve them in cold water acidulated with sulphuric acid. Add caustic soda, wash and filter as rapidly as you can, and dry the gelatinous mass on blotting-paper. When dry, heat some of the solid in a dry test-tube.

We note that the green gelatinous precipitate becomes much darker on drying; it turns black and gives off water when heated, leaving at last a brown solid.

Exp. 293.—Repeat the previous experiment, using ferric sulphate instead of ferrous, and washing the precipitate before drying it on blotting-paper. Dry some of the precipitate on the water bath and heat in a dry test-tube, as before.

We note that the brown gelatinous precipitate gives off water when heated, and leaves a red powder; also that the precipitate dried at 100° C. still contains water.

The percentage composition of the oxides of iron can be determined by passing pure hydrogen over weighed quantities and finding the loss of weight, that is the loss of oxygen. The experiment is carried out in a similar manner to that of the determination of the composition by weight of water (Exp. 112), except that it is not necessary to weigh the water formed, and the tube containing the reduced iron must be carefully corked or stoppered while cooling. The ferric oxide is observed to turn black at first and then gradually to become the grey metal as the temperature is raised much higher.

In the case of ferric oxide, the percentage composition is found to be—

Iron	=	70·0
Oxygen	=	30·0
		100·0

From this we can calculate the weight of iron which combines with 8 gm. of oxygen, *i.e.* an equivalent of iron $= \frac{8 \times 70}{30} = 18{\cdot}7$.

An equivalent of iron found from the oxide obtained from the green sulphate is found to have a different value approximating to 28, so that iron would appear to have two different equivalents.

This is confirmed by determining an equivalent of iron by displacement of hydrogen from dilute hydrochloric acid as in Exp. 114. In this experiment green ferrous chloride is formed and an equivalent of 28 is confirmed for iron when it forms ferrous salts.

230. The Atomic Weight of Iron.—In making chemical analyses and using their results we find that we require for accurate work the true atomic weights of the elements, and these have been determined in different ways. The preceding experiments show that iron differs from the other metals we have examined in forming two kinds of sulphates, green and brown respectively, and that each kind of salt has a corresponding oxide and hydroxide of corresponding colour; also that iron has different equivalents in the green and brown compounds respectively.

In our previous work we have defined the atomic weight of an element as the smallest weight of that element which can take part in a chemical change, taking the molecular weight of hydrogen as 2 and its atomic weight as 1. It follows that the atomic weight of an element is the smallest quantity of that element found in a molecular weight of any of its compounds. The metallic compounds, however, are not generally easily converted into vapour of which we can find the density, but we may use the fact that the atomic weight = equivalent weight × a whole number, so that if we take the least common multiple of 28 and 18·7 we obtain 56, which may be used as the atomic weight of iron.

Another method of determining the probable atomic weight of a metal is based on the fact, discovered by Dulong and Petit, that the specific heat of the metal × its atomic weight = 6·4 (on an average). Since the specific heat of iron is about ·112, its atomic weight should be about $\frac{6{\cdot}4}{{\cdot}112}$ = about 57, so the true atomic weight must be either $28 \times 2 = 56$ or $18{\cdot}7 \times 3 = 56$.

This value for the atomic weight of iron is confirmed by other methods which we need not consider further.

231. Formulae of Iron Compounds.—Since ferrous oxide contains 28 gm. of iron combined with 8 gm. of oxygen, 56 gm. of iron must combine with 16 gm. of oxygen, and the formula becomes FeO. The formula of ferrous hydroxide becomes $Fe(OH)_2$.

Similarly, since ferric oxide contains 18·7 gm. of iron combined with 8 gm. of oxygen, 56 gm. of iron must combine with 24 gm. of oxygen = 16 × $1\frac{1}{2}$ or $1\frac{1}{2}$ atomic weights of oxygen. We have decided that the atom is the smallest portion of an element which can enter into a chemical compound, so we must multiply by 2, that is 2 atoms of iron combine with 3 atoms of oxygen in forming ferric oxide. The formula of ferric oxide thus becomes Fe_2O_3, and of ferric hydroxide, $Fe(OH)_3$.

Both of these oxides are basic oxides, and the formulae of the sulphates may be inferred from their formation, thus:—

$$FeO + H_2SO_4 = H_2O + FeSO_4$$

$$Fe_2O_3 + 3H_2SO_4 = 3H_2O + Fe_2(SO_4)_3.$$

We have already noted (Exp. 287) that the green crystals of ferrous sulphate contain water; they are represented by the formula $FeSO_4, 7H_2O$. Ferric sulphate also contains water of crystallisation, but it is not very definite in quantity, so that the solid is usually represented as $Fe_2(SO_4)_3$.

[A curious commercial practice may be noted, by which ferric sulphate is frequently sold as nitrate of iron.]

232. Magnetic Oxide of Iron.

Exp. 294.—Heat a bright piece of iron, *e.g.* a knife blade, in the flame for some time, and note the effect. Drop some iron filings through a flame and examine the product, testing it with a magnet.

We note that iron burns in air, forming a hard black powder, which must be an oxide, and is magnetic. This is a third oxide of iron; it is called the *magnetic oxide of iron* and is represented by the formula Fe_3O_4. A valuable ore of the metal, called *magnetite*, consists mainly of this oxide.

Exp. 295.—Dissolve some magnetic oxide of iron in hydrochloric acid, and test it with caustic soda, potassium ferricyanide, and potassium sulphocyanide.

We observe that a black precipitate is formed with caustic soda, and that both ferrous and ferric salts are present. The magnetic oxide in fact acts like a mixture of ferrous and ferric oxides, and may be written Fe_2O_3, FeO. The oxide is of definite composition and acts as a feeble compound of two other oxides, and since both oxides (FeO and Fe_2O_3) act as basic oxides and form corresponding series of salts, the action of acids upon the magnetic oxide produces two different salts at the same time, one salt corresponding with each basic oxide.

The magnetic oxide of iron is also formed when red-hot iron decomposes steam with the formation of hydrogen.

233. The Preparation of Iron.—The reduction of iron oxide by carbon monoxide is the basis of the commercial preparation of iron from its ores, which consist generally of either ferric oxide or substances which easily yield ferric oxide when heated. The ore is mixed with coke and limestone, and placed in a furnace, the *blast furnace*. When the coke is lit, air is blown through the fire. Carbon dioxide is first formed and is reduced to the monoxide by the red-hot carbon. The monoxide reduces the oxide of iron, becoming itself the dioxide, and the process repeats itself. The sand and clay and other impurities present in the ore are removed by the limestone, which forms with them a fusible glass or slag. The iron melts, collects below the melted slag, and is run out and cast into "pigs." It is called *pig iron*, and contains 2 to 5 per cent. of carbon, together with smaller quantities of phosphorus, sulphur, and silicon. If part of this carbon is removed, we obtain steel, containing 0·5 to 2 per cent. of carbon, and finally wrought iron with less than 0·5 per cent. of carbon. [*Note.*—If the iron ore is a pure oxide, then the carbon monoxide produces pure wrought iron at once.]

The reduction can be represented by the equation

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2.$$

The properties of these kinds of iron are of very great commercial importance: cast iron is hard, brittle, melts at a bright red heat, and expands on solidifying; steel is also hard, but tough and elastic, and it can also be melted and cast; wrought iron is softer, very tough, and cannot readily be melted; it is also fibrous in structure, and not crystalline.

234. The Chlorides of Iron.—The salts of iron can also be readily examined by means of the action of hydrochloric acid.

Exp. 296.—Dissolve iron filings in hydrochloric acid as in Exp. 286, and examine the green crystals formed as in Exp. 289, using nitric acid and silver nitrate as a test for a chloride instead of barium chloride in test (v). Pass chlorine through the green solution and over metallic iron; dissolve the brown product formed in the latter case in water and test both solutions obtained as before. Also boil the brown solution with iron and hydrochloric acid, applying the tests as before. Lastly, dissolve ferric oxide in hydrochloric acid, and examine the reaction and the products obtained.

We note that iron forms a green crystalline solid, and also a brown powder, both of which are chlorides of iron.

The relationship between the chlorides is similar to that between the sulphates, and the precipitate produced by caustic soda solution shows that both the green salts correspond with ferrous hydroxide and oxide, while both the brown salts correspond with ferric hydroxide and oxide.

We also note that in this case the oxidation of ferrous to ferric chloride can be brought about by the direct addition of chlorine to ferrous chloride, and the reduction by the direct addition of iron to the ferric chloride. The formula given to ferrous chloride is $FeCl_2$, or in the crystalline form $FeCl_2, 6H_2O$, while that given to ferric chloride is $FeCl_3$. In both cases the vapour density confirms the formulae assigned to the dry chlorides. The latter salt forms brown solids containing different amounts of water, which cannot be definitely represented by a formula.

Equations which represent the changes above considered are :—

$$Fe + 2HCl = FeCl_2 + H_2$$

$$2Fe + 3Cl_2 = 2FeCl_3$$

$$Fe_2O_3 + 6HCl = 2FeCl_3 + 3H_2O$$

$$2FeCl_2 + Cl_2 = 2FeCl_3$$

$$2FeCl_3 + Fe = 3FeCl_2.$$

Assuming these formulae for the chlorides of iron, we can infer those of the hydroxides prepared by the action of caustic soda solution upon them, thus :—

$$FeCl_2Aq + 2NaOHAq = Fe(OH)_2 + 2NaClAq$$

$$FeCl_3Aq + 3NaOHAq = Fe(OH)_3 + 3NaClAq.$$

235. The Rusting of Iron.

Exp. 297.—Take five watch glasses and place on each a heap of clean iron filings. Moisten (i) with distilled water; leave (ii) dry; moisten (iii) and place it in an atmosphere of carbon dioxide by standing it on a glass plate under a bell jar beside a small beaker containing marble chips and dilute sulphuric acid; moisten (iv) and place it in an atmosphere free from carbon dioxide by standing it in the same way as (iii) beside a little beaker containing a solution of caustic soda under a bell jar; place the last (v) in a dry atmosphere free from carbon dioxide, by standing it under a bell jar beside a lump of quicklime. After a few days examine the rust formed in each case by dissolving it in dilute hydrochloric acid, and testing as in Exp. 289.

We notice that iron rusts more quickly in moist air than in dry, and more quickly in moist air containing carbon dioxide than in air free from that gas, and that it does not rust at all in dry air free from carbon dioxide; it is probable, therefore, that the rusting of iron is generally brought about by the combined action of carbon dioxide and water, which produces a solution of the acid, carbonic acid, thus :—

$$H_2O\ Aq + CO_2 = H_2CO_3\ Aq.$$

This carbonic acid then attacks the iron in the same way as other acids.

Exp. 298.—Take two gas jars, wet them inside and sprinkle iron filings into them. Invert them over water saturated with carbon dioxide and over a solution of caustic soda respectively. Moisten a third jar with ammonium chloride solution, add iron filings, and invert over water. Note the changes and test the gas left in the jar in each case.

We note that the process of rusting removes oxygen from the air, so that it is a complicated process. We also note that rusting is much helped by the presence of a chloride, such as ammonium chloride or sodium chloride, so that in order to prevent agricultural implements from rusting they should be kept dry and washed free from chemical manures when not in use.

236. Iron Compounds and Agriculture.—Plant ash, fertile soil, and burnt animal tissues, such as dried blood, all contain sufficient iron to give the ordinary tests, and the iron is essential to life and growth. It is generally present in sufficient quantity in the soil to supply the needs of the plant, and in foodstuffs to supply the needs of the animal. The two series of iron salts differ in the fact that ferrous salts are generally poisonous, while ferric salts are beneficial; ferrous sulphate is used as a germicide. In an ordinary soil exposed to the air ferrous salts absorb oxygen and become ferric, as may be observed when blue clay is exposed to the air and turns brown; similarly, water trickling over blue limestone deposits, on evaporation, brown ferric oxide. Again, the magnetic oxide of iron occurs in some soils, and the ferrous oxide is only slowly oxidised. It is therefore necessary to be able to determine the amount of iron contained in the soil in both the ferrous and the ferric states.

237. The Estimation of Iron.—The oxidation of ferrous salts to ferric by the action of potassium permanganate solution already noted (Exp. 291) is found to be constant and gives a convenient method of estimating iron in solution in the ferrous state.

Exp. 299.—Weigh out 12·41 gm. of clear light green crystals of ferrous sulphate, or better 17·5 gm. of pure light green ferrous ammonium sulphate, pour into a 250 c.c. flask, add dilute sulphuric acid and water, making up the solution to the 250 c.c. mark with freshly boiled distilled water. Both these solutions contain 1 per cent. of iron in the ferrous state. Weigh out also 10 gm. of pure potassium permanganate and dissolve in a litre flask, making up to the mark; this is a 1 per cent. solution of potassium permanganate. Pipette out 20 c.c. of the iron solution, add a few c.c. of dilute sulphuric acid and run in the permanganate solution from a burette until there is just a very faint permanent tinge of pink colour. If the colour is brown and not pink, add more dilute sulphuric acid. Repeat.

In one series of experiments it was found that the number of c.c. of permanganate required averaged 11·2.

Now 20 c.c. of 1 per cent. iron solution contain ·2 gm. Fe, and this is oxidised by 11·2 c.c. of 1 per cent. potassium permanganate, *i.e.* by ·112 gm.

Therefore 56 gm. Fe in the ferrous state use, for oxidation to the ferric state, $\frac{\cdot 112 \times 56}{\cdot 2} = 31{\cdot}4$ gm. of the permanganate.

We can write an equation to represent the oxidation from our knowledge of the formulae of ferrous and ferric sulphates if we assume that potassium permanganate has the formula $KMnO_4$ or, as it is frequently written doubled, $K_2Mn_2O_8$, and that when it loses its excess of oxygen in presence of sulphuric acid, the manganese (atomic weight = 55) forms a sulphate represented by the formula $MnSO_4$.

Taking the doubled formula

$$2K + 2Mn + 8O = 2 \times 39 + 2 \times 55 + 8 \times 16 = 316.$$

We have found that 31·4 gm. of permanganate oxidise 56 gm. of iron, so that 314 gm. would oxidise nearly 560 gm. of iron (= 10Fe) from the ferrous to the ferric state. An equation which expresses this fact is

$$10FeSO_4 + K_2Mn_2O_8 + 8H_2SO_4$$
$$= 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O,$$

and this equation can be used for other solutions.

Ferrous sulphate is sometimes used as an adulterant to other dearer salts, and may be estimated by the preceding reaction.

Exp. 300.—Weigh out accurately about 5 gm. of green vitriol, dissolve it in a 100 c.c. flask with dilute sulphuric acid, and fill up with water to the mark. Mix well and pipette out 20 c.c. of the solution, add dilute sulphuric acid, and run in 1 per cent. permanganate solution from the burette until the solution just turns pink.

In one experiment exactly 5·015 gm. of green vitriol were weighed out, and the average number of c.c. of 1 per cent. permanganate solution required was found to be 10·7. The calculation is as follows:—

20 c.c. of iron solution were oxidised by 10·7 c.c. of 1 per cent. permanganate solution, *i.e.* by ·107 gm. $K_2Mn_2O_8$.

By the equation

$$10FeSO_4 + K_2Mn_2O_8 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O,$$

316 gm. $K_2Mn_2O_8$ oxidise 560 gm. iron from the ferrous to the ferric state.

$$\therefore \text{ 20 c.c. iron solution contain } \frac{\cdot107 \times 560}{316} \text{ gm.,}$$

$$\text{and 100 c.c. iron solution contain } \frac{\cdot107 \times 560 \times 5}{316} \text{ gm.}$$

$$= \cdot948 \text{ gm. ferrous iron.}$$

That is

5·015 gm. of green vitriol contain ·948 gm. of ferrous iron, and the percentage of ferrous iron in the green vitriol analysed

$$= \frac{\cdot948 \times 100}{5\cdot015} = 18\cdot9.$$

The percentage of ferrous iron in pure ferrous sulphate is 19·8, so that the specimen taken contains $\frac{18\cdot9}{19\cdot8} \times 100 =$ 95·5 per cent. of pure $FeSO_4$, $7H_2O$.

Exp. 301.—Boil some soil with concentrated hydrochloric acid and test the solution for ferrous and ferric iron as in Exps. 292 and 293.

It is generally found that soils give with hydrochloric acid a solution which contains iron, but almost entirely in the ferric state. The iron contained in such a solution cannot be estimated by oxidation with potassium permanganate, since it is already oxidised, so that it is necessary, if we are to use permanganate, that the iron should be reduced to the ferrous state without loss. Further, oxidation by the air must be prevented, as well as any decomposition of the permanganate other than by the ferrous iron present.

The reduction can be effected in acid solution by means of zinc, when part of the hydrogen which would be set free combines directly with the excess of oxygen in the ferric salt, reducing it completely to ferrous; hydrogen acting thus is called *nascent.* If hydrochloric acid is used the reduction may go further when the acid is neutralised and metallic iron may be replaced, but if dilute sulphuric acid is used this does not so easily happen. The reaction with the permanganate takes place more satisfactorily in presence of sodium sulphate, or better, manganese sulphate.

Exp. 302.—Weigh out accurately about 20 gm. of iron ammonium alum, warm with dilute sulphuric acid until dissolved, and dilute to the mark with water in a 250 c.c. flask. Fit up each of three 4 oz. flasks with a cork carrying a glass tube about 2 in. long, on to which is fitted about an inch of rubber tubing in which a slit has been cut with a sharp knife, as indicated in Fig. 85. Close the open end of the rubber tube with a piece of glass rod about half an inch long. Such an arrangement is called a *Bunsen valve,* and allows gases and steam to pass out from the flask but not inwards.

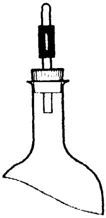
Fig. 85.

Pipette off 20 c.c. of the solution into each flask, add dilute sulphuric acid and 4 or 5 pieces of granulated zinc free from iron. Allow the action to go on for about 10 minutes and test if all the iron is reduced by taking a filter paper, dipping it in ammonium sulphocyanide solution and touching the paper with a glass rod which has been dipped into the solution in the flask and quickly removed. When the spot on the paper is colourless or only faintly pink all the iron has been reduced.

Take a pinch of glass wool and screw it into the neck of a funnel standing over a beaker; rapidly pour the contents of the flask on the glass wool and rinse the flask and wool once or twice with water. Now run in 1 per cent. permanganate solution from a burette until the usual pink colour is seen.

In one experiment, 20·44 gm. of the iron ammonium alum were weighed out, and the average number of c.c. of the permanganate required was 10·7. The calculation, carried out exactly as in the preceding experiment, showed the percentage of iron to be 11·59. This iron was present as a compound of ferric oxide, Fe_2O_3, so that the percentage of ferric oxide was 16·56.

Iron ammonium alum containing when pure 11·62 per cent. of iron is the most convenient ferric compound of fixed composition which is soluble in water or dilute sulphuric acid. Soils and iron compounds must generally be dissolved in strong hydrochloric acid after weighing, made up to the fixed volume, and reduced by zinc and dilute sulphuric acid as in the last experiment, with the addition of 2 or 3 grams of sodium sulphate or manganese sulphate to avoid the reduction of potassium permanganate by the hydrochloric acid.

Mixtures of ferrous and ferric compounds of iron can also be estimated by finding first the amount of ferrous iron and then the total amount of iron after reduction by zinc and dilute sulphuric acid : the difference will be the amount of ferric iron.

Exp. 303.—Estimate the amount of ferrous and ferric iron in magnetic oxide of iron, grinding it as finely as possible and dissolving in hydrochloric acid. Add sodium or manganese sulphate before running in the permanganate solution.

238. Aluminium.—Aluminium is a white metal, only about 2·7 times as heavy as water, and with an atomic weight of 27.

Exp. 304.—Examine the action of water, hydrochloric acid, and caustic soda solutions on aluminium foil, without and with the addition of a few drops of mercury or mercuric chloride solution.

We note that aluminium has little action on water or hydrochloric acid, but that it is attacked by soda ; when the aluminium is in contact with mercury, *i.e.* amalgamated, the action becomes energetic.

Aluminium compounds are poisonous, so that food should not be kept long in contact with the metal in presence of alkali.

239. Aluminium Oxide.

Exp. 305.—Make a solution of aluminium in hydrochloric acid with a few drops of mercuric chloride solution, or boil china clay with fairly strong sulphuric acid, cool, and carefully dilute. Add to the solutions (i) ammonia, (ii) caustic soda in excess, and add to (i) and (ii) ammonium chloride solution in excess.

We note that both ammonia and soda give a white gelatinous precipitate soluble in excess of the reagent and reprecipitated by the addition of ammonium chloride. The precipitate is aluminium hydroxide, represented by the formula $Al(OH)_3$, which on being heated gives off water, and is converted into aluminium oxide or *alumina*, represented by Al_2O_3.

Aluminium hydroxide acts as a base and dissolves in acids forming ordinary salts; thus the formation of the chloride is represented by the equation

$$Al(OH)_3 + 3HCl = 3H_2O + AlCl_3.$$

The hydroxide also dissolves in caustic soda forming salts of another kind in which it acts as an acid. These salts are called *aluminates*, and the caustic soda reaction is represented by the equation

$$Al(OH)_3 + 3NaOH = 3H_2O + Al(ONa)_3.$$

Hydroxides which have this property are called *amphoteric* hydroxides.

Exp. 306.—Make an extract of soil with boiling hydrochloric acid and add ammonium chloride and ammonia. Filter off the precipitate and wash it. Pour a solution of caustic soda on the precipitate and test the filtrate by adding ammonium chloride in excess.

We note that, while the ferric hydroxide remains on the filter paper, sodium aluminate passes through, and from this aluminium hydroxide is precipitated by ammonium chloride. This forms our *test for aluminium.*

The ordinary salts of aluminium, in which the hydroxide acts as a base, are, perhaps, not of general interest in agriculture, with the exception of common alum, aluminium phosphates, and aluminium silicates.

240. Common Alum.—Common alum is made by crystallising together aluminium sulphate, prepared as above, with potassium sulphate. The crystals are large and have a definite shape (octahedral) and a constant composition. They are represented by the formula K_2SO_4, $Al_2(SO_4)_3$, $24H_2O$. Their solution gives the usual tests for potassium, aluminium, sulphuric acid, and water, and they form what is called a *double salt.*

Exp. 307.—Add to white of egg solution some alum solution.

We note that a precipitate of insoluble albumen is formed, and alum is used to precipitate and harden proteins so as to prevent decomposition.

241. Phosphates of Aluminium and Iron.

Exp. 308.—Just neutralise solutions of aluminium and ferric chlorides with ammonia and add sodium phosphate.

We note that precipitates are formed of aluminium and ferric phosphates respectively: they may be represented by the formulae $AlPO_4$ and $FePO_4$ respectively, and are of importance owing to their insolubility. Soluble phosphatic manures gradually lose their solubility in the soil, as they become changed into these two salts.

242. Silicates of Aluminum and Iron. Clays.—In Exp. 305 we noted that pure china clay (kaolin) contains alumina as a base, and in Exp. 251 we found silica in soils: ordinary clay soils contain ferric oxide as well as alumina. Clays generally are silicates of alumina and iron combined with varying quantities of water which gives them their peculiar character. A general formula has been conveniently adopted to include most common clays, viz.:

$$x\,Al_2O_3,\ y\,SiO_2,\ z\,H_2O,$$

in which x, y, and z are whole numbers; the aluminium may be replaced wholly or partly by iron, and the hydrogen in the water molecules wholly or partly by sodium, potassium, calcium, or magnesium. The retention of the bases of manures by the soil is largely a question of replacement of hydrogen in the water molecules.

CHAPTER XX.

CAPILLARY PHENOMENA: SURFACE TENSION.

243. Supply of Water to Crops.—All our farm crops require a large quantity of water for their successful growth; thus in producing 1 lb. of dry matter the cereals use over 250 lb. of water and the cruciferous plants as much as 900 lb. Calculated in another way, a crop of wheat yielding 20 bushels per acre has used about 6 inches of rain, and a crop yielding 40 bushels per acre requires about 12 inches of rain.

In the Eastern Counties, with an average rainfall of 25 inches a year, only about 10 inches falls during the growing season of the wheat, and is unevenly distributed through the season, so that the extra requirements must be supplied by the soil.

Though the rain falling on ordinary soil is generally rapidly absorbed, the Rothamsted rain gauges show that it takes a very long time to fall through even 4 feet of soil under the action of gravity. Now, water rises in the soil in dry weather against the action of gravity, so that the cause of the delay is not likely to be due to simple friction.

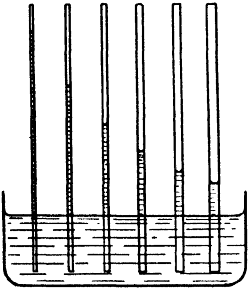
Fig. 86.

244. Capillary Phenomena.

Exp. 309.—Draw out some glass tubing in a flame so as to make tubes of small diameter about 6 in. long and from about $\frac{1}{8}$ in. in diameter downwards. Stand them upright in a basin of coloured water and observe what takes place (Fig. 86).

We note that the water rises in the tubes against the attraction of gravity above the level in the beaker, and that the rise is greater the smaller the diameter of the tube.

Exp. 310.—Take two glass plates about 3 to 4 in. square, put a match stalk between two edges and tie the plates together so as to form a wedge-shaped space between the plates, and stand in the coloured water with the edges which are in contact upright (Fig. 87).

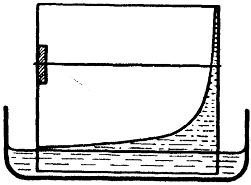

Fig. 87.

We note that tubes are not necessary to enable the water to rise, and that between plates it rises higher where the space between the plates is narrower.

Exp. 311.—Cut a block of common table salt about 1 in. square and 6 in. long, and stand it upright in the coloured water.

Dip the lower end of a piece of lamp wick into methylated spirit in a beaker.

Take a glass tube about $\frac{1}{2}$ in. in diameter and tie a piece of muslin or calico over the end. Put some dry soil into the tube, tap the tube to make the soil settle, and stand upright in the coloured water.

We note in each case that the liquid rises above its level in the beaker, and that it rises at different rates and to different heights through the air spaces between the salt crystals, cotton fibres, and soil particles. The rise is chiefly evident when the tubes or spaces are small, and it is said to be due to *capillarity*.

245. Surface Tension.—The property of rising against gravity would seem to be imparted to the liquid by the small spaces or tubes, but it might also be due to the liquid itself.

Exp. 312.—Repeat Exps. 309 and 310, having previously greased or oiled the tubes and plates. Also repeat these experiments, using mercury instead of water.

We note that instead of rising in the tubes and between the plates, both the water and the mercury are pressed down below the level of the rest of the liquid, so that the rise takes place only in a space which the liquid can wet.

Exp. 313.—Roll several sheets of blotting or filter paper into cylinders and secure them with cotton or string. Stand three of these cylinders upright in different beakers containing (*a*) coloured water, (*b*) coloured methylated spirit, (*c*) soap solution.

We note that the heights to which the liquid rises are different in the three cases, though the paper is the same, so that the rise appears to be connected with the liquid. The property seems to be in some way connected with the surface of the liquid. The surface also resists the downward flow of the liquid.

Exp. 314.—Remove the capillary tubes used in Exp. 309 from the liquid, keeping them upright.

Make a small sieve from very fine wire gauze (100 meshes to 1 inch) and pour some water into it. Examine the under surface. Then touch the under side with a wet finger.

Thread a piece of string through 3 or 4 small indiarubber balls and dip them in (*a*) water, and (*b*) oil, and suspend them over the vessels containing the liquids.

We note that the capillary tubes are not completely emptied but that some liquid remains in each, above a partly formed drop with a convex spherical curve (Fig. 88 (*a*)). We see also that the sieve can apparently hold water until it is wetted underneath; the liquid as at first seen from underneath is protruding in tiny hemispherical bags between the wires (Fig. 88 (*b*)), but these run together when rubbed and the water drops through.

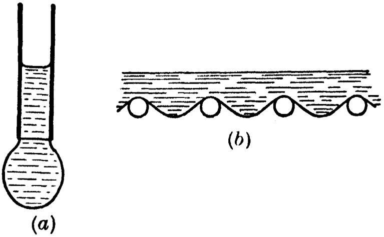

Fig. 88.

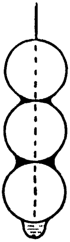

Fig. 89.

In the third case the liquids are seen to cover the balls and to form a neck between each pair of balls; the neck gradually diminishes in diameter between the upper balls and finally when the balls are nearly dry almost disappears; the necks are curved so as to be concave towards the liquid (Fig. 89).

These observations can be explained if we assume that the surface of a liquid is in a state of stretch or tension similar to the state of a piece of stretched indiarubber sheet.

Exp. 315.—Blow out a small indiarubber balloon, blow a soap bubble*, and then uncover the end of the tube or pipe in each case. Also examine the formation of drops from a burette.

We note that in all three cases the spherical form is taken, and that in the first two cases pressure is exerted by the sphere on the contained air. This can take place if the liquids exert a tension similar to that of the indiarubber, and this tension is called the *surface tension* of the liquid.

In the preceding experiments the force or tension exerted by the liquid is applied at the point of contact of the liquid with the solid, and is able to pull or draw the liquid up until the tension is balanced by the weight of the liquid. The smaller the radius of the curved surface the greater is the resultant effect of the tension.

If the above explanation is correct, then altering the surface of the liquid ought to affect the surface tension.

Exp. 316.—Float a dry wire gauze sieve made as in Exp. 314 on the surface of some water and pour some vapour of ether into the sieve.

Cover a porcelain plate with some coloured water such as a solution of potassium dichromate and drop one drop of ether into the middle. Note the effect.

Put a mixture of alcohol and water into a small beaker, wet the sides with the mixture, and stand in the air.

In the first case the ether vapour weakens the surface tension of the water, and the sieve sinks.

In the second case the higher surface tension of the water tears the surface away from the ether drop, leaving a clear centre.

In the third case the spirit and water, which start as a uniform layer, are seen to separate out into streaks and drops

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* A good solution for this purpose is made by dissolving 1 gm. of sodium oleate or Castile soap in 100 c.c. of water with the addition of a small quantity of glycerin.

(tears of strong wine). This is due to the more rapid evaporation of the spirit, which allows the water with the stronger surface tension to pull itself into streaks and form drops.

We are therefore led to the conclusion that the surface of a liquid is in a state of tension, *surface tension*, which enables the liquid to crawl along any surface it can wet, and that the effect of the different sized tubes and air spaces is simply to allow this surface tension to act as an ordinary force with components inclined at different angles.

246. Comparison of Surface Tensions.—The surface tensions of liquids can be compared by noting the rise of the liquids in the same capillary tube after making allowance for their densities.

Exp. 317.—Select a capillary tube of uniform bore, break it into two parts, and hold the two tubes upright with their lower ends dipping into water and alcohol respectively. In each case measure the height of the column of liquid in the capillary tube above the surface of the liquid in the vessel.

Then

$$\frac{\text{Surface tension of alcohol}}{\text{Surface tension of water}}$$

$$= \frac{\text{Height of alcohol column} \times \text{density of alcohol}}{\text{Height of water column} \times \text{density of water}}.$$

Surface tensions are measured in units of force exerted per centimetre of the line of contact of the liquid and solid, and in the case of water the surface tension may be taken for purposes of comparison as 80, that is 80 dynes per cm.

Another convenient method of comparing surface tensions is by comparing the weights of drops of liquids passing through the same jet under the same pressure.

Exp. 318.—Fill a burette up to any mark, say 20 c.c., with water. Weigh a small beaker, place it under the burette, and turn the tap so that the water drops slowly into the beaker, say at a rate of about 2 drops a second. Count 100 drops and weigh. Empty the burette, wash it out with 1 per cent. soap solution and fill up with the soap solution to the same mark as before. Run 100 drops of the solution into the beaker and weigh again.

Then $$\frac{\text{Surface tension of soap solution}}{\text{Surface tension of water}}$$

$$=\frac{\text{Weight of 100 drops of soap solution}}{\text{Weight of 100 drops of water}}.$$

247. **Effects of Surface Tension.**—Since the height to which water can climb in a soil depends on the size of the air spaces in the soil, and that is determined by the size of the soil particles, the height to which water can rise in a clay soil is much greater than in a sandy soil, and it has been found that water can climb 8 feet above the water table in a clay soil. The holes are very small, however, so that the water can only rise very slowly. The ordinary acts of cultivation are largely directed to influencing the supply of water to the growing plant, and to preventing loss by evaporation by cutting the small tubes and so preventing the escape of the water. Thus rolling tends to bring the water towards the surface, and ploughing, cultivating, and hoeing to prevent the loss of water.

248. **The Surface of a Liquid.**—A great deal of attention has been directed to the reasons why liquid surfaces should have their peculiar properties, and it seems probable that the peculiarities are caused by the large number of molecules which strike the surface and do not succeed in passing through it into the air, but are reflected or retained there. As the temperature of the liquid rises, more molecules are able to get out into the air, and the surface tension falls. In solutions it has been found in many cases, as for instance in soap solutions, that the surface tension slowly changes to a constant value, suggesting that the dissolved molecules are elongated instead of spherical, and gradually succeed in packing themselves with their longer axes more or less at right angles to the surface, when they have the greatest effect. A complete explanation will no doubt shortly be reached.

CHAPTER XXI.

SOME IMPORTANT SUBSTANCES.

249. Copper Compounds.—Copper is a reddish metal with an atomic weight of 63. Its compounds have a very important poisonous action on fungoid diseases of plants and animals, but as copper is also poisonous to living matter in general, the compounds are used as washes or in sprays. The sulphate is used as a wash for foot rot in sheep, and the hydroxide and carbonate as a preventative of potato disease and vine diseases.

Exp. 319.—Examine the reactions of copper when heated alone, and with strong and weak hydrochloric, nitric, and sulphuric acids, also with caustic soda (or potash) and ammonia solutions.

We note that copper turns black when heated in air, dissolves in nitric acid of all strengths forming a blue solution, dissolves in hot, strong, sulphuric acid giving a dirty grey residue, and in ammonia forming a violet solution, but it is insoluble in hydrochloric acid, dilute sulphuric acid, and soda.

250. The Preparation and Properties of Copper Sulphate.

Exp. 320.—In an evaporating basin place about 10 c.c. of strong sulphuric acid and a quantity of copper turnings. Heat the basin in a draught chamber and add more copper as long as it dissolves. When the product is nearly dry allow it to cool, and when cold add water. Boil, filter, and evaporate until crystals appear; allow the solution to evaporate slowly and form large crystals. Dry the crystals, dissolve some, and test them with barium chloride solution, with ammonia solution, and with a strip of iron. Repeat the experiment, using copper oxide instead of copper. Compare the crystals.

The crystals in both cases contain copper and are sulphates, so that they contain a sulphate of copper, which we may represent by the formula $CuSO_4$.

Exp. 321.—Weigh out about 2 gm. of powdered copper sulphate crystals in a weighed crucible and heat carefully over a flame, stirring occasionally and taking care that the crucible does not become red-hot. (A better way is to heat the crystals in an air oven at about 230° C.) Cool and weigh again.

Calculate the loss per cent., and then calculate the water combined with $63 + 96 = 159$ gm. of copper sulphate and divide by 18, as in Exp. 218.

We find that the crystals of copper sulphate contain five molecular weights of water to one of the sulphate, and are therefore represented by the formula $CuSO_4, 5H_2O$. We also note that the blue crystals become colourless when they lose water, and we have already used the regeneration of the blue colour by the addition of water as a test for the latter substance.

251. The Action of Alkalies on Salts of Copper.

Exp. 322.—To dilute solutions of sulphate of copper add excess of (i) caustic soda, (ii) ammonia, (iii) sodium carbonate. Note the formation of any precipitates. Boil the liquids and note any change. Test the precipitates for sulphuric acid. Repeat the experiments, but filter off the first precipitates and dry them on blotting-paper. Then warm them in test-tubes and note any changes.

We note that cold solutions of all three reagents give blue gelatinous precipitates; the precipitate from soda or ammonia is the base, copper hydroxide $Cu(OH)_2$. The precipitate from the carbonate is a carbonate containing excess of the base or less acid than would be required for complete substitution of the OH groups of the base, and is called a basic carbonate, generally represented by the formula, $CuCO_3Cu(OH)_2$ or $Cu_2(OH)_2CO_3$. The hydroxide is slightly soluble in excess of soda but easily soluble in excess of ammonia, yielding a deep violet solution. The precipitate given on boiling the solution, when adding soda, is black and is the oxide, CuO, into which the hydroxide also turns on standing.

In making sprays for attacking potato disease, etc., copper hydroxide is used in *Bordeaux mixture* and copper carbonate in *Burgundy mixture*, but it is important to precipitate all the copper from solution.

The formation of the violet colour with ammonia is a *general test for copper.*

252. Lead Compounds.—Lead is a heavy white metal with an atomic weight of 207, which readily tarnishes in air, and is rapidly oxidised in the molten condition. The oxide formed is called *litharge*, and is represented by the formula PbO. Lead compounds are poisonous to animal and plant life.

253. Reactions of Lead.

Exp. 323.—Examine the reactions of lead and litharge with strong and dilute hydrochloric and nitric acids, hot and cold.

We note that lead is slightly soluble in hot concentrated hydrochloric acid, forming on cooling a small quantity of crystals, which are like the crystals formed by dissolving lead oxide in hot hydrochloric acid. Lead dissolves readily in nitric acid, both concentrated and dilute, on warming, but only slowly in the cold, nitrous fumes being formed.

Exp. 324.—To a solution of lead oxide in nitric acid, (i) add hydrochloric acid and cool under the tap, (ii) add dilute ammonium sulphide solution.

We note that lead chloride is insoluble in cold water, and is precipitated on the addition of hydrochloric acid to a solution containing lead; also that a brown colour or precipitate is given with ammonium sulphide. The formation of the brown colour and the formation of a white precipitate with hydrochloric acid, insoluble in cold but soluble in hot water, and reprecipitated in a crystalline form on cooling, make satisfactory *tests for lead.*

Exp. 325.—Add to a solution of lead in nitric acid or of lead nitrate (i) caustic soda solution, (ii) sodium carbonate. Filter off and dry the precipitates and then heat them over a flame.

We note that white precipitates are formed in each case, and that both are converted into yellow fusible litharge when heated. The former precipitate is the base, lead hydroxide, represented by $Pb(OH)_2$, and the latter lead carbonate, represented by the formula $PbCO_3$.

254. Red Lead.

Exp. 326.—Put a small quantity of red lead into a test-tube, add hydrochloric acid and test the fumes with potassium iodide and starch paper. Allow the solution to cool.

We note that lead chloride is formed and chlorine given off. We have also noted (Exp. 29) that red lead gives off oxygen when heated; it leaves yellow litharge, so that it is an oxide of lead which contains more oxygen than litharge. Such an oxide is called a *peroxide*, and the oxide containing relatively less oxygen is said to be a *lower oxide* than the other; a metallic peroxide may thus be defined as *an oxide which reacts with acids to form a salt corresponding with a lower oxide of the metal, and at the same time yields oxygen or some oxidised product of the acid.* The formula assigned to red lead is Pb_3O_4.

Exp. 327.—Place in two flasks (i) a strip of lead half covered with distilled water, (ii) a similar strip of lead and hard water. Shake from time to time and test some of the liquid every day with hydrochloric acid, with dilute ammonium sulphide, and with litmus paper: compare the results.

We note that lead is acted upon in the air by distilled water, and that the lead hydroxide formed is slightly soluble in pure water, forming a milky alkaline solution. This solution reacts with hard water containing calcium bicarbonate in solution, forming an insoluble lead carbonate.

255. White Lead.—White lead is prepared by the action of carbon dioxide and vinegar vapour on strips of lead. The metal gradually becomes converted into white lead, which is then finely ground.

Exp. 328.—Place some powdered white lead in a test-tube and add hydrochloric acid. Test any gas given off by lime water. Boil the mixture and filter hot. Note what takes place.

White lead contains carbon dioxide and forms lead chloride with hydrochloric acid, so that it is a carbonate of lead. It is a basic carbonate, and may be represented by the formula $2PbCO_3, Pb(OH)_2$. It possesses the poisonous properties of other lead compounds, and is used in making paints.

256. Arsenic Compounds.—Owing to their poisonous character arsenic compounds are used on the farm in the form of sheep dips and arsenical sprays for killing caterpillars in orchards.

Arsenic is largely derived from its sulphides, which are found either in a pure state or mixed with tin and copper ores. When these compounds are roasted in the air the arsenic is generally volatilised and becomes oxidised, condensing in the form of *white arsenic,* the common commercial source of arsenic compounds.

257. Oxides of Arsenic.

Exp. 329.—Place a few grains of white arsenic in a test-tube and heat in a flame. Examine the condensed vapour under a microscope.

We note that the arsenic volatilises without melting, a process which is called *sublimation*, and that the condensed vapour or *sublimate* is made up of small shining white crystals with eight faces, *i.e.* octahedra.

Exp. 330.—Heat a few grains of white arsenic with powdered charcoal in a narrow test-tube. Heat the black sublimate and allow it to condense on the upper part of the tube.

Exp. 331.—Boil a few grains of white arsenic in a test-tube with a strip of clean copper foil and strong hydrochloric acid. Wash and dry the strip and heat it in a test-tube. (Reinsch's test.)

We note that in both cases a black volatile substance is produced, and that this easily oxidises when heated in air to give a white crystalline sublimate.

The black substance is an element, *arsenic*, represented by the symbol As, and having an atomic weight of 75. The crystalline oxide, white arsenic, is represented by the formula As_2O_3, and is called *arsenious oxide.* The formation of the black stain and sublimate by reduction, and of the white sublimate by oxidation, is a very delicate *test for arsenic.*

Exp. 332.—Test the reactions of arsenious oxide with (i) water, (ii) litmus solution, (iii) hydrochloric acid, cold and hot, and (iv) caustic soda solution.

We note that arsenious oxide is not very soluble in water, and has an acid reaction; it dissolves, however, in hot hydrochloric acid and in caustic soda, so that it appears to resemble alumina in being able to act as both a basic and an acid oxide.

It is not a strong base, though it can make sulphates.

Equations representing the above changes are

$$As_2O_3 + 6HCl = 3H_2O + 2AsCl_3$$

$$As_2O_3 + 2NaOH = H_2O + 2NaAsO_2.$$

The salts in which arsenious oxide acts as an acid oxide are called *arsenites*, and one of them, the arsenite of copper, represented by the formula $CuHAsO_3$, is used as an insecticide, under the name of *Scheele's* or *Paris green*.

Exp. 333.—To a solution of sodium arsenite add copper sulphate. A green precipitate of Paris green is formed.

Exp. 334.—Warm a few grains of arsenious oxide with nitric acid. Evaporate the product to dryness on a water bath and test for nitrates. Test some of the solid with litmus, with magnesia mixture, and by boiling with ammonium molybdate solution. Heat some of the solid nearly to redness in a dry test-tube.

We note that large volumes of nitrous fumes are given off from the nitric acid, and the residue contains only a trace of nitrate, so that the nitric acid appears to be used up in oxidising the arsenious acid in some way, without forming a salt.

The white powder is strongly acid and has properties similar to those of phosphoric acid; it also gives off water on heating. The powder is found to be an acid represented by the formula H_3AsO_4 and called *arsenic acid*, which is converted when nearly red-hot into the oxide represented by As_2O_5, called *arsenic pentoxide*.

The conversion of arsenious into arsenic oxide is quantitative and will be examined later. Arsenic acid combines with bases forming *arsenates*.

Exp. 335.—Neutralise some of the arsenic acid with caustic soda solution and evaporate a portion to dryness. Add to some of the neutral solution (i) calcium chloride solution, (ii) lead acetate solution.

We note that arsenic acid forms a soluble sodium salt, sodium arsenate, Na_3AsO_4, and insoluble calcium arsenate,

$Ca_3(AsO_4)_2$, and lead arsenate, $Pb_3(AsO_4)_2$. The latter salts have been used as insecticides in spraying fruit trees, but as arsenic acid resembles phosphoric acid in forming soluble acid arsenates resembling superphosphates, special care has to be taken in the precipitation, and the use of calcium arsenate has been given up.

258. Sulphides of Arsenic.—Two important ores of arsenic are the sulphides, *realgar*, a red solid represented by the formula As_2S_2, and *orpiment*, a bright yellow solid represented by the formula As_2S_3, which thus corresponds in composition with arsenious oxide, As_2O_3. Both sulphides burn readily when heated in a flame, forming arsenious oxide and sulphur dioxide.

The disulphide, realgar, is decomposed by acids and alkalies yielding arsenic and derivatives of the trioxide.

The reactions of the trisulphide are of interest.

Exp. 336.—Dissolve a few grains of arsenious oxide in hydrochloric acid, or add hydrochloric acid to a solution of sodium arsenite: (i) pass into the solution sulphuretted hydrogen gas, (ii) gradually add a solution of yellow ammonium sulphide.

We note that a yellow precipitate is produced in both cases, and that it is insoluble in hydrochloric acid but soluble in excess of yellow ammonium sulphide. This yellow precipitate is arsenious sulphide, with the same composition as orpiment, As_2S_3.

Exp. 337.—Shake up some orpiment or the precipitated sulphide with caustic soda or ammonia, and add hydrochloric acid to the solution.

The solid goes into solution and is reprecipitated by hydrochloric acid. The solution contains a double sulphide of arsenic and sodium or ammonium, together with an arsenite. The soluble double sulphide in the first case is represented by the formula $NaAsS_2$, which resembles the arsenite $NaAsO_2$, and is called sodium thioarsenite or sodium sulpharsenite.

Exp. 338.—To a solution of sodium arsenate add excess of yellow ammonium sulphide, and to the solution add hydrochloric acid.

We note that a yellow precipitate is formed, resembling the trisulphide but rather paler in colour. This precipitate is a pentasulphide of arsenic, represented by the formula As_2S_5, and corresponding with arsenic pentoxide, As_2O_5. The solution of the sulphide in ammonium sulphide contains a double sulphide which may be represented by the formula $(NH_4)_3AsS_4$ and resembles the phosphate $(NH_4)_3PO_4$, so that the double salt is called ammonium thioarsenate or ammonium sulpharsenate. Arsenic in solution in the form of these double sulphides is very poisonous, and is used, especially in the form of sheep dips, to destroy maggots and insect pests.

259. **Bromine.**—When sea water is evaporated, common salt first crystallises out, and the solution contains magnesium chlorides and other very soluble salts. Similarly, when the potash salts are crystallised out from the crude salt obtained from their natural salt beds they leave very soluble salts in solution. These residues have an interesting reaction, most simply observed in the case of potassium bromide.

Exp. 339.—To a few crystals of potassium bromide in a test-tube add strong sulphuric acid and warm. Test the fumes with litmus paper.

We note that acid white fumes resembling hydrochloric acid are first given off, and that the fumes shortly turn orange. The orange fumes condense to a dense orange-brown liquid with a strong and unpleasant smell. [N.B.—Great care must be taken not to inhale these fumes and not to allow the liquid to touch the skin.] This liquid is an element closely related to chlorine, and called *bromine*. It is represented by the symbol Br, and has an atomic weight of 80. The white fumes formed at the same time as the bromine are those of *hydrobromic acid*, represented by the formula HBr, and having properties similar to those of hydrochloric acid. Hydrobromic acid combines with bases forming *bromides*, thus with caustic potash potassium bromide is formed; the reaction may be represented by the equation

$$HBr + KOH = H_2O + KBr.$$

Exp. 340.—To a solution of potassium bromide add (i) silver nitrate solution, and then ammonia in excess, (ii) chlorine water followed by boiled starch solution.

We note that the silver nitrate gives a yellowish white precipitate only soluble in a very large excess of ammonia, and that chlorine water turns the solution orange from the separation of the characteristically smelling bromine, and that the starch is also turned orange. These are *tests for bromides and for free bromine*, and the chlorine appears to be able to displace bromine from bromides.

Exp. 341.—Carefully drop one or two drops of bromine into a solution of caustic soda. Test with litmus solution, turkey red cotton, and a ferrous salt. Put a small quantity of paraffin wax in a test-tube, melt it, and drop in one drop of bromine.

We note that bromine dissolves in caustic soda solution to from a strongly oxidising solution resembling bleaching powder solution, and that it combines with paraffin wax forming hydrobromic acid fumes which contain hydrogen which it must have obtained from the wax. The solution in caustic soda contains a salt, *sodium hypobromite*, represented by the formula $NaBrO$. The last two reactions are of great importance in the study of organic chemistry.

260. Iodine.—The ash prepared from the stalks of many large seaweeds is of interest, and may be more easily examined in the form of a salt, potassium iodide.

Exp. 342.—To a few crystals of potassium iodide in a test-tube add strong sulphuric acid, and warm. Test the fumes with litmus paper.

We note that heavy acid white fumes resembling hydrochloric acid are given off in small quantity, and that the crystals then turn brown, and give off violet fumes which condense in the upper part of the test tube in the form of shining black scales, and have a pungent characteristic smell.

This solid is an element, closely related to bromine and chlorine. It is called *iodine* and is represented by the symbol I, and has an atomic weight of 127. The white fumes are those of *hydriodic acid*, represented by the formula HI, and having properties similar to those of hydrobromic and hydrochloric acids.

Sodium nitrate, as prepared in Chile, is separated from the surface soil in which it occurs by dissolving in water and crystallising out by concentration. When sulphurous acid or, better, sodium bisulphite, is added to the residue of the concentrated solution, a brown precipitate is formed which is filtered off, and consists of iodine. The sulphurous acid or sulphite is found to be oxidised to sulphuric acid or a sulphate, so that the iodine probably existed in the form of an oxide or acid oxide. It is found that the salt present has a composition similar to that of sodium nitrate and potassium chlorate; it is called *sodium iodate*, and is represented by the formula $NaIO_3$.

Exp. 343.—Test the solubility of iodine in (i) water, (ii) a solution of potassium iodide, (iii) chloroform or ether, (iv) carbon disulphide. [N.B.—In the last case be very careful not to carry out the experiment anywhere near a flame or fire, and do not pour the liquid down the drain, except in a stream of water.]

We note that iodine dissolves slightly in water, readily in potassium iodide solution, chloroform, and ether, forming an orange brown to brown solution, and in carbon disulphide forming a violet solution.

Exp. 344.—To a solution of potassium iodide add (i) silver nitrate solution, followed by excess of ammonia, (ii) chlorine water, followed by a few drops of starch paste; boil (ii), then cool in water.

We note that silver nitrate gives a yellow precipitate insoluble in ammonia, and that chlorine water displaces iodine, which forms a blue colour with starch paste, discharged on boiling but restored by cooling.

In chlorine, bromine, and iodine we have a case of three elements which resemble one another in character and properties. Chlorine is a gas, bromine a liquid, and iodine a volatile solid; all three form hydrides which are acid and form similar salts, and all form oxides of similar composition which are acid oxides. These three elements are in consequence said to form a *group* called the *halogens;* compounds of the halogens are called *haloid* compounds.

The halogens are all of importance to living matter; thus salt is required by animals for digestion, and iodides in small quantity seem to be needed to assist in such purposes as the maintenance of health and the deposit of good shells on eggs.

261. Quantitative Reactions of Iodine.—The formation of hydriodic acid from iodine by combination with hydrogen derived from water is quantitative, and leads to many interesting oxidations.

Exp. 345.—Weigh out carefully 2·5 gm. of pure dry iodine and put into a 250 c.c. flask. Add about 4 gm. of pure potassium iodide and about 50 c.c. of distilled water. When all the iodine is dissolved, fill up to the mark.

Weigh out carefully 2·5 gm. of pure arsenious oxide, put it into a 250 c.c. flask, and carefully add caustic soda solution until the arsenious oxide is dissolved. Then add about 20 gm. of sodium bicarbonate and fill up to the mark with distilled water.

Pipette out 10 c.c. of the arsenic solution into a beaker and run in the iodine solution from a burette until the solution is just tinged yellow. Add a few drops of starch paste to make sure that the yellow colour is due to free iodine, and test the solution for arsenates.

In one experiment the volume of iodine solution required was 25·5 c.c.

Since both solutions are 1 per cent., ·10 gm. of arsenious oxide is oxidised by ·255 gm. of iodine.

Now the formula weight of arsenious oxide, As_2O_3, is $2 \times 75 + 3 \times 16 = 198$, so that the number of gm. of iodine required to oxidise 198 gm. of arsenious oxide to arsenic pentoxide $= \frac{198 \times {\cdot}255}{{\cdot}10} = 505$ gm. $= 4 \times 127$ nearly, or 4 I. We can thus express the reaction quantitatively by the following equation :—

$$As_2O_3 + 4I + 2H_2O = As_2O_5 + 4HI.$$

Many oxidising agents liberate iodine quantitatively from acidified potassium iodide, and on distillation, the iodine may be absorbed by potassium iodide solution, made up to a known volume, and estimated by arsenic as above.

There are other salts which reduce iodine quantitatively to hydriodic acid, *e.g.* sodium sulphite and bisulphite, and more especially sodium thiosulphate (the photographic *hypo*), which is represented by the formula $Na_2S_2O_3, 5H_2O$, and is easily obtained in the form of pure crystals.

Exp. 346.—Make 250 c.c. of a 1 per cent. solution of pure crystals of sodium thiosulphate as before, adding a small quantity of sodium bicarbonate to the solution before making up to the mark. Pipette out 20 c.c. and run in 1 per cent. iodine solution from a burette as in the previous experiment, until a faint yellow tinge, turned blue by starch paste, is observed.

In one experiment the volume of 1 per cent. iodine solution required was 20·5 c.c.

Since both solutions are 1 per cent., ·20 gm. of sodium thiosulphate is oxidised by ·205 gm. of iodine.

That is, the weight of sodium thiosulphate oxidised by one atomic weight of iodine $= \frac{127 \times \cdot 20}{\cdot 205} = 124$ gm.

Now $Na_2S_2O_3, 5H_2O$ has a formula weight of 248, so that the oxidation of the formula weight of the salt requires 2×127 gm. of iodine $= 2$ I.

An equation made to represent the oxidation quantitatively is

$$2Na_2S_2O_3, 5H_2O + 2I = Na_2S_4O_6 + 2NaI + 10H_2O,$$

in which the salt represented by $Na_2S_4O_6$ is called *sodium tetrathionate.* This reaction is more generally used for estimating iodine than the previous one.

262. Normal and Decinormal Solutions.—In estimating the amount of any substance contained in a solution when using methods of back titration it sometimes saves time and calculation if we make up our standard solutions in such a way that equal volumes of every solution are equivalent. Such solutions, containing one equivalent weight of acid, alkali, silver, etc., dissolved in a litre of water, are called *normal solutions*, and if they contain $\frac{1}{10}$ of an equivalent weight per litre they are called *decinormal solutions*, and so on.

The equivalent weights are calculated from the equations which are found to represent the reactions, taking, in the case of acids and alkalies, the weight containing one gram of replaceable hydrogen or the weight required to replace one gram of hydrogen. In the case of silver solutions the weight which will precipitate 35·5 gm. of chlorine is used, and in oxidising and reducing solutions, either the weight which will give up 8 gm. of oxygen or the weight which will absorb 8 gm. of oxygen is weighed out.

Such solutions require careful adjustment to make them exactly equivalent, and frequently require the use of a factor for accurate work, so that they are not generally required by the occasional worker who has, in any case, to check his work by the appropriate equation.

In commercial work it is general to use standard solutions of such a strength that 1 c.c. will indicate 1 mg. of the substance being estimated.

[*Note.*—It is important to note that the use of standard solutions for obtaining accurate results in chemical analysis depends upon the accuracy with which they can be made in the first place. Comparatively few acids and alkalis are of 100 % purity, so that for accurate work, when the principles of the methods of *volumetric analysis* are understood, it is necessary to prepare at least one standard solution and compare the others with it. The following are generally used :—

For *acid and alkali estimations: Sodium carbonate* solution as prepared in Exp. 220, or containing 5·3 gm. Na_2CO_3 per litre for a decinormal solution.

For *iron estimations: Potassium permanganate* solution carefully prepared as in Exp. 299, or containing 3·16 gm. $KMnO_4$ per litre for a decinormal solution.

For *chloride estimations: Silver nitrate* solution carefully prepared as in Exp. 223, or containing 17·0 gm. $AgNO_3$ per litre for a decinormal solution.]

CHAPTER XXII.

ORGANIC COMPOUNDS: PURIFICATION AND ANALYSIS: VALENCY.

263. Organic Compounds.—In examining the action of heat on plant structures we have noted that water, ammonia, tar, and charcoal are formed, and that when the charcoal burns away an ash is left. If the experiment is repeated with meat or animal substances much the same changes are noticed. Now if hay or meat is burned in a stream of air the products which can be identified appear to be generally confined to water, ammonia, and carbon dioxide, while the ash usually contains compounds of sulphur and phosphorus, together with salts of calcium, sodium, and potassium. It seems probable, therefore, that the various products, other than the ash, can contain only the four elements, carbon, oxygen, hydrogen, and nitrogen, in chemical combination, and that the compounds we meet in plant and animal structures must be built up out of these four elements, which, by the variety of their compounds, are able to make up for the smallness of their number.

Organic Chemistry, or the chemistry of plant and animal products, is thus fundamentally the chemistry of the four elements, carbon, oxygen, hydrogen, and nitrogen, and includes the study of the molecules which can be built up from these elements as well as the study of the products obtained by decomposing the molecules of natural plant and animal products, so that a clear idea of the nature of the molecule, of the molecular and atomic theory (see Chapters IX. and X.), and of the determination of molecular weights is of primary importance in this subject.

264. Natural Organic Compounds.—The number of organic compounds available for investigation is so large that it is difficult to decide at what point to begin. We have plant and animal structures which are obviously mixtures ; we have the direct products of living matter both soluble and insoluble in water, *e.g.* starch, sugar, essential and other oils, etc. We have also products of fermentation and putrefaction, *e.g.* spirit, vinegar, etc., but we should perhaps expect that the products obtained from organic compounds by the action of heat (*destructive distillation*), are likely to be simpler in character than those from which they are derived. We meet such products in the distillation of coal, oil shale, petroleum, and wood.

265. Fractional Distillation.—These natural organic compounds are generally impure, and it becomes necessary to purify the bodies before attempting to examine them with a view to identification. The operations are, on the whole, as general as the methods available in inorganic chemistry. For instance, we employ *distillation.*

Exp. 347.—Place a mixture of methylated spirit and water (one to two) in a distilling flask connected with a condenser, and provided with a cork through which a thermometer is fixed, in such a position that its bulb is just below the side exit tube. Support the apparatus by a retort stand, place a burner under the flask and a receiver under the end of the condenser tube, and note the rise of the thermometer. When the liquid boils it rises at once

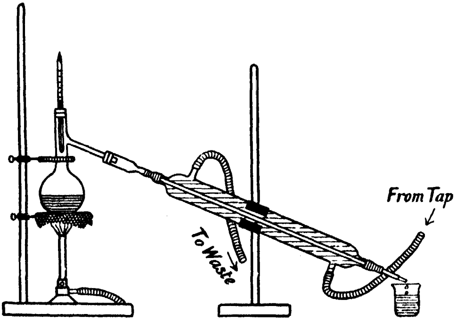


Fig. 90.

to about 79·5° C. and remains at that point for a short time; it then gradually rises until it reaches nearly 100° C. Change the receiver when the temperature begins to rise above about 85° C., and again at about 99° C. In this way the mixture is separated into three parts or fractions which boil at different temperatures. Try to light some of the original and the fractions. Only the first fraction burns and this contains the greater part of the spirit.

The process just described is called *fractional distillation*, and is largely used in separating mixtures of liquids.

266. The Use of Solvents.—The method of purification by solution and filtration or crystallisation is similar to that in use in inorganic work, except that the number of solvents available is much greater in organic work. Alcohol, ether, chloroform, acetic acid, benzene, petroleum, and sometimes glycerin, are used, in addition to water. Since these bodies are not equally soluble in each other, separation is sometimes effected by taking a substance which is dissolved or disseminated in one liquid out of that liquid by means of another liquid, *i.e.* the method of *extraction* by shaking with ether or chloroform.

Exp. 348.—Place some milk in a cylinder and add to it some caustic soda solution and some ether, and shake well. Allow to stand; in a short time the ether will rise to the surface. Pipette off a few drops and put them on blotting paper.

The drops evaporate, leaving spots of grease behind, thus showing that the fat contained in the milk has been dissolved out by the ether.

267. Test for the Purity of Organic Compounds.—Every pure substance which is not decomposed by melting or boiling has a definite melting point or boiling point or both, and traces of impurities cause changes in these temperatures. Thus the melting point is usually lowered and the boiling point raised by impurities. If the liquid is a mixture of two different liquids, the boiling point is generally between those of the two liquids and gradually rises as in Exp. 347.

The test for purity of a preparation is thus to find out whether its melting point or its boiling point is changed by further purification, *e.g.* recrystallisation or redistillation.

The determination of melting and boiling points has already been described in Chap. VIII., Arts. 95 and 97.

268. Testing for the Elements contained in Organic Compounds.—The tests which are available for the bodies separated and purified by any method are quite general, and consist in the first place of the characteristic reactions of the chief elements.

Exp. 349.—Take some powdered pure copper oxide, heat it to redness in a crucible, and allow it to cool in a desiccator. Mix with it a little sugar and heat the mixture in a hard glass tube. Test the liquid which is formed by means of anhydrous copper sulphate. Also lower a drop of lime-water into the tube on a glass rod.

The anhydrous copper sulphate turns blue, showing that water has been formed from sugar and the dry copper oxide; this proves the presence of *hydrogen* in the sugar. The lime water is turned milky, hence carbon dioxide is present, and must have come from *carbon* in the sugar.

Exp. 350.—Take a small piece of gelatin, put it in a test-tube, add a small piece of sodium about the size of a pea and heat very carefully. When the action stops put the tube into a larger tube or beaker and add water, ferrous sulphate, ferric chloride, and hydrochloric acid.

The formation of a blue colour, Prussian blue, shows that *nitrogen* has been contained in the gelatin. (See pp. 340, 341.)

The halogens may be identified by heating the substance with pure quicklime, dissolving in dilute nitric acid and testing by silver nitrate solution. (Art. 117.)

Sulphur and phosphorus may be identified by fusing some of the substance with potassium nitrate and then testing for a sulphate or phosphate respectively.

Exp. 351.—Take a little white of egg, mix it with potassium carbonate, and heat. When the reaction is over place the residue on a silver coin and moisten with dilute hydrochloric acid.

A black stain of silver sulphide is formed, showing the presence of *sulphur*.

269. Determination of Percentage Composition.—Modifications of the above methods of testing for the elements are used to determine the quantitative composition of organic bodies. To determine the percentage of carbon and hydrogen, a weighed quantity of the body is mixed with excess of copper oxide and heated in a long glass tube, or it is heated in a stream of oxygen which is then passed over red-hot copper oxide. The water and the carbon dioxide formed are collected in a calcium chloride tube and a solution of caustic potash, respectively, and weighed. Then since 44 grams of carbon dioxide contain 12 grams of carbon, and 18 grams of water contain 2 grams of hydrogen, the carbon in the weighed substance $= \frac{12}{44} = \frac{3}{11}$ of the weight of carbon dioxide, and the hydrogen in the weighed substance $= \frac{2}{18} = \frac{1}{9}$ of the weight of water. In this reaction any nitrogen present is evolved in a free state and may be collected and measured after passing through caustic potash solution to absorb carbon dioxide. The details of organic analysis, *i.e.* the *carbon and hydrogen* and the *nitrogen combustion* are beyond the scope of this work, as are also numerous methods of determining nitrogen, sulphur, phosphorus, the halogens, etc.

270. Vapour Densities.—The next step in the determination of the molecular composition of a compound is the determination of its vapour density, the relation of which to the molecular weight of a substance was discussed in Chapter IX., Art. 112., when we came to the conclusion that the molecular weight of any substance, taking the molecule of hydrogen as having a molecular weight = 2, is equal to twice the vapour density of the substance as compared with the vapour density of hydrogen taken as = 1,

or $$m = 2d.$$

Now while some organic compounds are gases, a very large proportion of them are liquids or solids, and can be converted into vapour without decomposition. Many methods of determining vapour densities are available, but generally two are used, based on the definition

$$\text{density} = \frac{\text{mass}}{\text{volume}}.$$

The first method is to find the weight (mass) of a known volume of the vapour somewhat as in Exp. 37 ; this is called *Dumas's method.* The second method is to find the volume occupied by a known weight (mass) in the state of vapour, and is called *Victor Meyer's method.* Both these methods are outlined below.

In *Dumas's method,* a bulb, holding about 300 c.c., with a long drawn-out neck is used. The bulb is weighed and a few grams of the substance are inserted in it. The bulb is then heated to a known temperature above the boiling point of the substance in a bath of water, oil, or other liquid, until the substance is all converted into vapour and stops blowing out of the neck. The neck is then sealed and the bulb cooled, cleaned, and weighed. The neck is then broken off and the bulb filled with water, whose volume is determined by measuring or weighing. The difference between the weighings of the bulb before and after heating is the difference between the weight of the volume of the vapour filling the bulb at the temperature and pressure of the experiment, and that of the air filling the bulb at the start and displaced by the vapour.

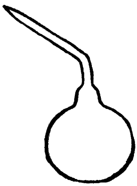


Fig. 91.

The original weight of the air must, therefore, be added to the observed difference after correcting the volume of the vapour and of the air for their respective temperatures and pressures. The vapour density is finally calculated as the corrected weight of 11·2 litres of the vapour at 0° C. and 760 mm. pressure.

In *Victor Meyer's method,* a small quantity of the substance (about ·2 gm.) contained in a small glass tube is dropped into a long glass tube with a bulb at the end, which is heated by steam, aniline, or fusible alloy, as in Fig. 92. The substance is rapidly converted into vapour, which expels an equivalent volume of air through a side delivery tube. The expelled air is collected and measured. The hot air expelled from the bulb corrects its volume for temperature as it rapidly cools, so that it is only necessary to correct for the temperature and pressure of the air of the laboratory. Knowing the volume of vapour obtained from the known weight of the substance, the vapour density is calculated as before.

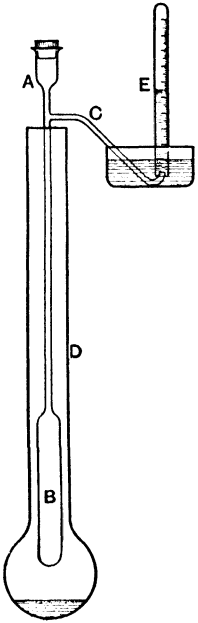


Fig. 92.

271. Determination of Molecular Compositions and Molecular Formulae.—From the percentage composition and the molecular weight of a body it is possible at once to calculate the molecular composition and the molecular formula by a general method.

1. From the percentage composition calculate the composition of such a weight of the substance as contains at least 1 gram of hydrogen, 16 grams of oxygen, or 12 grams of carbon.

2. Divide the molecular weight by the sum of the weights of the component elements as found above, (1), and find the nearest whole number to the quotient.

3. Multiply each item of the percentage composition found in (1) by the whole number found in (2), and the molecular composition is obtained.

4. Divide the quantity of each element in the molecular composition by its atomic weight in the usual way, and obtain the number of atoms of each element in the molecule.

Examples are given later.

272. Valency.—A consideration of the volume changes in the reactions of gases (as in Chapter X.) led to the recognition of the existence of smaller parts within the molecules, viz. the *atoms*, so that molecules are built up of atoms held together by some attractive force which is electrical in character, and is generally called chemical affinity.

Now some molecules contain only two atoms, *e.g.* H_2, Cl_2, HCl, O_2, and in these we can only assume that each atom acts on the other, but in the case of other molecules with three or more atoms, *e.g.* H_2O and NH_3, we have greater possibilities, as each atom may attract both or all the others or one atom may attract all the others. We get out of this difficulty when we look more closely into molecular compositions and notice that a single hydrogen or chlorine atom is never combined with more than one other atom. We also notice that one oxygen atom generally combines with two other atoms, one nitrogen atom with three or five others, and one carbon atom with four others. We call this property of atoms their *valency*, and we agree to define it as a number representing the maximum number of atoms which the atom we are considering can attract or hold together to form a molecule. The atoms of chlorine and hydrogen are thus our *standard monovalent atoms*.

The question of valency is of the utmost importance in organic chemistry, since the combination of atoms into molecules is determined by valency.

CHAPTER XXIII.

HYDROCARBONS : PARAFFIN SERIES.

273. Constituents of Coal Gas.—To begin our investigations of organic compounds we might start with the gas prepared by the decomposition of hay or vegetable matter, but we can more easily obtain in quantity a similar gas, coal gas, and we test this first of all by burning.

Exp. 352.—Collect a cylinder of coal gas (which has been passed over caustic soda to remove carbon dioxide and through sulphuric acid to remove water) by upward displacement and apply a light to it.

The gas burns and the product left in the cylinder turns lime-water milky. We note that water is formed as well. Coal gas, then, contains combined carbon, and hydrogen combined or free, perhaps both. If the gas is passed through a long porous tube or over spongy platinum—or better, palladium—about forty per cent. is found to be absorbed as free hydrogen. The residue still forms carbon dioxide and water on burning. If the residual or original gas is allowed to stand over strong sulphuric acid about eight per cent. of the original volume disappears, but the fifty per cent. of the original gas which is left still contains carbon and hydrogen. The properties of this residual gas are similar to those of a gas prepared from vinegar by heating it with excess of soda lime, or better from sodium acetate by heating it with soda lime.

274. Marsh Gas or Methane.—The analysis of the residual gas of Art. 273 obtained by burning it with red-hot copper oxide gives the following percentage :—

$$\begin{array}{ll} \text{Carbon} & = 75{\cdot}00 \\ \text{Hydrogen} & = 25{\cdot}00 \\ \hline & \quad 100{\cdot}00 \end{array}$$

which, when arranged in terms of one part by weight of hydrogen is

$$\begin{aligned}\text{Carbon} &= 3\\ \text{Hydrogen} &= \underline{1}\\ &\ 4\end{aligned}$$

Now the vapour density of this gas is 8, so that the molecular weight of the gas is 16, and we must multiply each of the above figures by four to give the molecular composition; thus

$$\begin{aligned}\text{Carbon} &= 3 \times 4 = 12 = C\\ \text{Hydrogen} &= \underline{1} \times 4 = \underline{\ 4} = H_4\\ &\ 4 \qquad\quad 16\end{aligned}$$

The molecular formula of the gas is thus CH_4, and it is called *marsh gas* or *methane.* As it contains the least possible amount of carbon per molecule, *i.e.* one atom, it is looked upon as the simplest and most fundamental compound of carbon and hydrogen.

Methane or marsh gas is found in nature among the products of fermentation and decay in a limited supply of air, *e.g.* in the decay of vegetable matter under water in stagnant pools, marshes, and bogs. It is also found in coal mines as the explosive fire-damp, and in the natural gas of the oil districts.

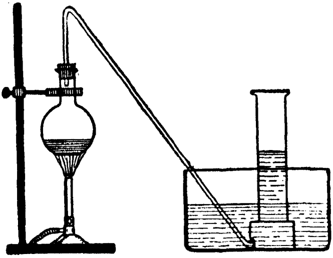


Fig. 93.

Methane is prepared in various ways, one of the most convenient being by the action of soda lime on sodium acetate.

Exp. 353.—Put some fused sodium acetate in a hard glass flask with excess of soda lime. Fit with delivery tube and arrange to collect the gas over water (Fig. 93). Heat the flask and collect the gas, after driving out the air. Care must be taken not to fuse the flask locally or to allow condensed water to run back on the hot parts. Notice the colour, taste, and smell of the gas, and test with a lighted taper. Prove that it is lighter than air by leaving a jar of the gas standing mouth upwards without a cover for a few moments, then testing with a lighted taper. Show also that the gas explodes when mixed with ten times its volume of air in a soda-water bottle. Prepare an extra cylinder for Exp. 354.

275. Use of Equations in Organic Chemistry.—Before writing an equation to represent this reaction it will be well to reconsider the subject of equations very briefly.

An equation should tell us as far as possible (i) the elements taking part in a reaction, their arrangement before and after the change, and the weights of the initial and final products; (ii) the volume of any gaseous constituents; and (iii) something (generally not much) about the conditions of the reaction. In inorganic chemistry these requirements are generally fairly fulfilled, but in organic chemistry they are not, because as a rule the product desired is only one of several, and may only represent a very small part of the total products. Though the use of equations in organic chemistry is subject to this defect it does enable the possible products of a reaction to be determined, after which further work is necessary to select the product required.

The equation generally given for the reaction between sodium acetate and soda lime is

$$\underset{\text{Sodium acetate}}{NaC_2H_3O_2} + NaOH = Na_2CO_3 + CH_4.$$

Even at this stage this equation suggests that the two carbon atoms in sodium acetate must have different properties.

276. Properties and Composition of Methane.—As was seen in Exp. 353, methane is a colourless, tasteless gas with a slight smell of coal gas; it can be liquefied by pressure and low temperature, and boils at − 164° C. It is about half as heavy as air, its vapour density being only 8 compared with that of air = 14·4. The gas burns in air.

When methane is mixed with excess of oxygen and exploded, a contraction is observed equal to twice the volume of the gas taken, and caustic potash absorbs from the residue a volume of carbon dioxide equal to the volume of the original gas. An examination of the products of explosion at 100° C. shows that a volume of steam is formed equal to twice the volume of the original gas, so that 1 c.c. of methane gives rise to 1 c.c. of carbon dioxide and 2 c.c. of steam.

Applying Avogadro's Law,

1 molecule of methane gives rise to 1 molecule of carbon dioxide
+ 2 molecules of steam.

Now each molecule of carbon dioxide contains one atom of carbon, and each molecule of steam contains two atoms of hydrogen, and there is no oxygen in marsh gas.

∴ 1 molecule of methane contains 1 atom of carbon
+ 4 atoms of hydrogen,

and the gas is represented by the formula CH_4. This gives another and independent proof of the composition of methane.

277. Action of various Reagents on Methane.

(*a*) Chlorine.

Exp. 354.—Mix a cylinder of methane with an equal volume of chlorine.

White fumes are seen in diffused daylight, while in bright sunlight the mixture explodes. The mixture also explodes under the influence of burning magnesium wire. The chlorine disappears and fumes of hydrochloric acid are seen. The products are hydrochloric acid gas, which is readily absorbed by water, and another colourless gas which is only slightly soluble in water. This gas burns to a mixture of carbon dioxide, steam, and hydrochloric acid, and the percentage composition and molecular weight are represented by the formula CH_3Cl; it is called *monochloromethane* or *methyl chloride*.

Bromine and iodine have little or no action on methane.

(*b*) Hydrochloric acid has no action.

(*c*) Sulphuric and nitric acids have no action unless above 150° C., and then the action is only slow.

(*d*) Caustic soda has no action.

(*e*) Oxidising and reducing agents do not affect the gas.

Since the molecule of the gas contains four hydrogen atoms combined with one carbon atom, the carbon atom is tetravalent, and it is only possible to obtain derivatives from it by replacing or *substituting* one or more of the hydrogen atoms by other monovalent atoms or groups, as in the above case by chlorine. In fact, the repeated action of chlorine yields the bodies represented by CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4.

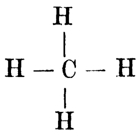
278. Synthesis of Methane.—There are many methods of preparing methane, which are of great interest, but need not be considered here. Some *syntheses* of methane which connect organic compounds with inorganic may, however, be mentioned.

(*a*) Hydrogen unites directly with carbon at 1200° C. to form methane.

(*b*) An electric spark passing between carbon poles in an atmosphere of hydrogen causes the formation of methane to the extent of $2\frac{1}{2}$ to 3 per cent. of the volume of the hydrogen.

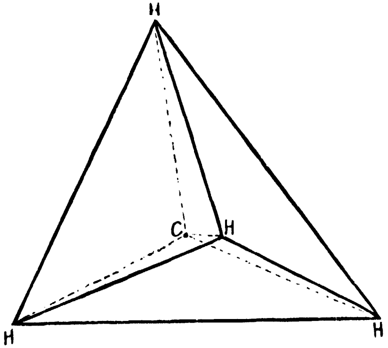
279. Constitutional Formula of Methane.—When the substitution derivatives of methane are carefully examined it is found that only one mono-substitution derivative, *i.e.* a compound formed by substituting one hydrogen atom by one monovalent atom or group, can be prepared. Thus it is possible to replace each of the hydrogen atoms in turn by chlorine, and the resulting monochloromethanes are identical.

Hence we assume that all the hydrogen atoms are symmetrically attracted by the carbon atom, and we draw a formula to represent this, in one plane, thus



$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H} - \mathrm{C} - \mathrm{H} \\ | \\ \mathrm{H} \end{array}$$

or in space by representing the carbon atom as the centre of a tetrahedron formed by the four hydrogen atoms, thus



These are *constitutional* formulae, and are of the greatest use. We must return to them later.

280. Ethane.—Starting with methyl chloride, CH_3Cl, it is possible to prepare an unlimited number of bodies. It is possible to remove the chlorine from the molecule by means of sodium. The methyl chloride is dissolved in ether and sodium is placed in the solution. A gas is given off which resembles methane in its reactions and is called *ethane*. By combustion its percentage composition and the amount required to contain one part by weight of hydrogen are found to be

$$\begin{array}{lrl} \text{Carbon} & = 80{\cdot}00 & = 4 \\ \text{Hydrogen} & = 20{\cdot}00 & = 1 \\ \hline & 100{\cdot}00 & = 5 \end{array}$$

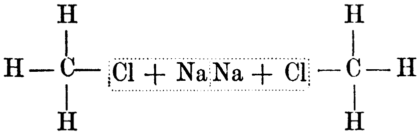
Its vapour density is 15, and its molecular weight is 30. Hence its molecular composition is

$$\begin{array}{lrcl} \text{Carbon} & = 4 \times 6 = & 24 & = C_2 \\ \text{Hydrogen} & = 1 \times 6 = & 6 & = H_6 \\ \hline & 5 \times 6 = & 30 & \end{array}$$

The formula C_2H_6 may be considered to be derived from CH_4 by (i) the substitution of a group of atoms CH_3 for one hydrogen atom, or (ii) the addition of a group CH_2. The former hypothesis is the only one which is consistent with the tetravalency of the carbon atom, so we must adopt it. Thus

$$CH_3Cl + CH_3Cl + 2\,Na = CH_3 - CH_3 + 2\,NaCl$$

The reaction may also be expressed structurally like this



$$H - \underset{H}{\overset{H}{C}} - \boxed{Cl + Na\,Na + Cl} - \underset{H}{\overset{H}{C}} - H$$

281. **Properties of Ethane.**—Ethane is a colourless, tasteless gas with a slight smell. It burns in air and explodes when mixed with air or oxygen. Chlorine acts upon it in sunlight, substituting one or more atoms of chlorine for hydrogen atoms as in the case of methane. The most interesting of these derivatives are *ethyl chloride* or monochlorethane, C_2H_5Cl, and the disubstituted compounds represented by the formula $C_2H_4Cl_2$, (see Art. 290.) The other reagents mentioned in Art. 277 do not attack ethane. Ethane resembles methane still further, as the methods of preparing methane are also generally applicable to ethane. Thus by distilling sodium propionate, a salt which contains three carbon atoms, with excess of soda lime we obtain ethane.

$$NaC_3H_5O_2 + NaOH = Na_2CO_3 + C_2H_6.$$

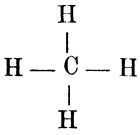
Perhaps the most important of the methods available is that by which we arrived at ethane, viz. the action of sodium on methyl chloride, since that method has enabled us to add a carbon atom to a molecule of a carbon compound.

282. **The Paraffin Series.**—The similarity of the properties of methane and ethane is generally connected with the presence in both molecules of carbon atoms which are tetravalent, and of tetravalent carbon atoms alone. We shall

find as we proceed that this intimate connection holds good. When the natural oil gas and the natural petroleum oils are distilled they may be separated into a large number of different fractions with approximately constant boiling points. Thus we can isolate bodies having the formulae C_3H_8, *propane*, C_4H_{10}, *butane*, C_5H_{12}, *pentane*, etc., up to bodies with fourteen or more carbon atoms in the molecule.

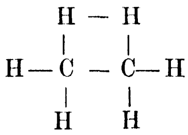
The properties of all of these bodies are similar to those of methane and ethane, and they differ in composition by the regular amounts of one carbon atom and two hydrogen atoms. If they are arranged in order of the number of carbon atoms in their molecules they form a series of which the earlier members up to pentane, C_5H_{12}, are gases at ordinary temperatures, from pentane to decane are liquids, and those with a higher carbon content are waxy solids. Such a series of bodies is called a *homologous series*, and this series is called the *paraffin series* since the members are so difficult to attack by reagents.

It will be noticed that the series is built up of carbon and hydrogen atoms, of which the hydrogen atoms are monovalent, so that they are held together by the attraction of each carbon atom for other carbon atoms, and must be assigned formulae to show this, thus



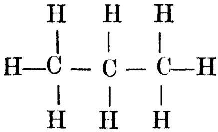
$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & — & C & — & H \\ & & | & & \\ & & H & & \end{array}$$

Methane.



$$\begin{array}{ccccccc} & & H & — & H & & \\ & & | & & | & & \\ H & — & C & — & C & — & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

Ethane.



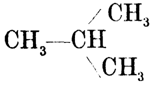
$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & — & C & — & C & — & C & — & H \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$$

Propane.

It is this extraordinary peculiarity of the carbon atom of combining with itself and forming new compounds, generally called *atom linking*, which makes the subject of carbon chemistry at the outset contrast so strongly with inorganic chemistry.

283. Isomerism.—Having once gained the idea that molecules can be built up by the linking of carbon atoms we are able to explain a further peculiarity noticed in the compounds of the paraffin series. When the hydrocarbons containing four or more carbon atoms are examined carefully, it is noticed that they have not always the same properties even with the same percentage composition and molecular weight. Thus in the case of *butane*, C_4H_{10}, we find two (but only two) bodies with different boiling points, − 17° C. and + 1° C., and forming different series of substitution derivatives.

An examination of the formula C_4H_{10} shows that it can be arranged in two ways and in two ways only, so as to keep the carbon atoms tetravalent and the hydrogen atoms monovalent : the two formulae are



$$\mathrm{CH_3{-}CH_2{-}CH_2{-}CH_3} \quad \text{and} \quad \mathrm{CH_3{-}CH}\begin{matrix}\diagup \mathrm{CH_3} \\ \diagdown \mathrm{CH_3}\end{matrix}$$

and each probably represents one of the known butanes. The former would be called *normal butane*, the latter *isobutane*. The existence of the two hydrocarbons and the two series of compounds is thus explained by the hypothesis of valency and the existence of the two formulae can be deduced on that hypothesis. The two butanes are said to be *isomers*, and we can define this phenomenon of *isomerism* thus :—When two compounds have the same molecular formula, but different properties, they are said to be *isomeric* with each other.

284. Occurrence and Preparation of Paraffin Hydrocarbons.—It should be noted that the natural oils and oil gas yield a large number of paraffins in their different fractions; thus the oil gas contains methane to butane and pentane ; gasoline and benzoline contain pentane to heptane ; paraffin oil contains heptane to decane ; and paraffin wax contains tetradecane and upwards. All these hydrocarbons and their isomers can be prepared by methods which are applicable to all. Thus we can (i) add one or more carbon atoms to any hydrocarbon by acting on a mixture of its monochloro derivative and methyl chloride (or iodide) by sodium, or (ii) take away one carbon atom by distilling with soda lime a salt of the acid formed from the hydrocarbon.

It is usual to call the substitution derivatives of organic compounds by chlorine, bromine, and iodine by the general name of *haloid* derivatives.

285. Haloid Derivatives of Methane.—Several of the haloid derivatives of methane are both interesting and important. We have seen already that chlorine reacts with marsh gas, forming in succession

Monochloromethane or methyl chloride.	CH_3Cl.
Dichloromethane or methylene dichloride.	CH_2Cl_2.
Trichloromethane or chloroform.	$CHCl_3$.
Tetrachloromethane or carbon tetrachloride.	CCl_4.

Methyl chloride, CH_3Cl, is more readily prepared by heating wood spirit, methyl alcohol, with concentrated hydrochloric acid under pressure, a reaction which may be represented by the equation

$$CH_4O + HCl = CH_3Cl + H_2O.$$

It is a gas liquefiable by pressure and is used in the preparation of organic compounds. The group of atoms $-CH_3$ which combines with the monovalent atom $-Cl$ to form methyl chloride is a monovalent group, the *methyl group*, a good example of an *organic radicle.*

286. Chloroform.—Chloroform, $CHCl_3$, is prepared by the action of bleaching powder on alcohol. It is a volatile colourless mobile liquid of specific gravity 1·527, boiling at 61° C. It dissolves fats and has a powerful anaesthetic effect.

Exp. 355.—Heat a few drops of chloroform with aniline and caustic soda solution and note the characteristic smell.

This characteristic smell, the *iso-nitrile* smell, gives a test for chloroform.

287. Carbon Tetrachloride.—CCl_4 is most readily prepared from carbon disulphide by passing chlorine through it. It is a colourless volatile mobile liquid with a smell similar to that of chloroform and with anaesthetic properties. It boils at 77° C.

288. Iodoform.—Another important haloid derivative of marsh gas is obtained by the action of iodine and caustic soda on alcohol. The action is similar to that of bleaching powder on alcohol, which produces chloroform.

Exp. 356.—Put into a test-tube some dilute alcohol and a few crystals of iodine. When the iodine has partly dissolved, add a few drops of a strong solution of caustic soda.

The colour of the solution turns to yellow, a solid separates out, and a characteristic smell is noticed. The yellow solid is *iodoform*, CHI_3. Iodoform is soluble in alcohol but so insoluble in water that its formation is used as a test for alcohol. It melts at 119° C. and decomposes at a higher temperature with the liberation of iodine.

CHAPTER XXIV.

HYDROCARBONS: ETHYLENE, ACETYLENE, BENZENE.

289. Preparation and Properties of Ethylene.—In the last chapter we removed chlorine from methyl chloride, CH_3Cl, by the action of sodium, but we can also remove it by the action of the hydroxide of sodium, caustic soda.

The methyl chloride, or better, methyl iodide, in solution in alcohol is warmed with the caustic soda, and a gas is given off which may be collected over water. The percentage composition and molecular weight of the gas are found to indicate the formula C_2H_4, and the gas is called *ethylene*.

Ethylene is generally and more easily prepared from alcohol by the action of sulphuric acid.

Exp. 357.—Make a mixture of 10 c.c. of alcohol (methylated spirit), 10 c.c. of water, and 30 c.c. of strong sulphuric acid, and place it in a glass flask fitted with a thistle funnel and a delivery tube for collecting over water (Fig. 94.). Heat the mixture to about 165° C. It froths and gives off ethylene gas. Collect four or five

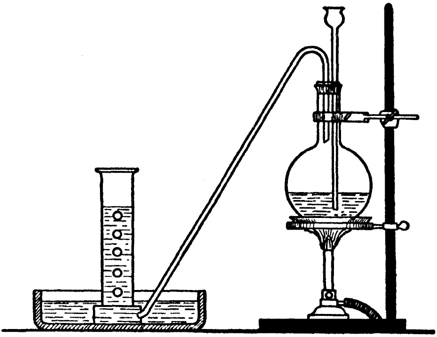


Fig. 94.

cylinders of the gas. (i) Turn one cylinder up and remove the cover. In a few seconds apply a light to it. The gas burns, it is not light enough to rise very quickly in air. (ii) Place one cylinder over a cylinder of equal size filled with chlorine. The gases disappear without forming hydrochloric acid and appear as oily drops (Dutch liquid). (iii) Drop a drop of bromine into another cylinder. The red colour disappears and oily drops are again found. (iv) Stand another cylinder over strong sulphuric acid. The gas is slowly absorbed by the acid.

Ethylene is a colourless gas with a slightly sweet spirituous taste and smell. It boils at – 103° C. It burns in air with a more luminous flame than methane, and explodes when mixed with three times its volume of oxygen. It combines directly with its own volume of chlorine or bromine vapour to form $C_2H_4Cl_2$ and $C_2H_4Br_2$, dichloro and dibromo ethane or *ethylene dichloride* and *dibromide* respectively. Ethylene combines slowly with hydrochloric acid and rapidly with hydriodic acid to form ethyl chloride and iodide respectively; it combines with sulphuric acid forming ethyl hydrogen sulphate. Oxidising agents oxidise it and reducing agents reduce it to ethane. It thus differs widely in its properties from ethane, which does not combine with reagents, and can only be changed by substitution.

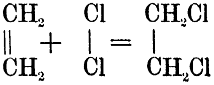
The reaction by which it is prepared is important and will be discussed later, but briefly, the formation of ethylene is due to the decomposition of a salt, ethyl hydrogen sulphate, which is formed by the reaction between the sulphuric acid and alcohol. The reaction may be represented by the equations

$$C_2H_6O + H_2SO_4 = \underset{\text{Ethyl hydrogen sulphate}}{C_2H_5 . HSO_4} + H_2O$$

$$C_2H_5 . HSO_4 = C_2H_4 + H_2SO_4$$

290. Dichloro Ethanes.—When ethylene and chlorine are brought together in equal volumes, they combine with the formation of a dichloro ethane, *ethylene dichloride*, $C_2H_4Cl_2$, which from its mode of formation must be $CH_2Cl - CH_2Cl$.

The equation representing its formation may be given as



$$\begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array} + \begin{array}{c} Cl \\ | \\ Cl \end{array} = \begin{array}{c} CH_2Cl \\ | \\ CH_2Cl \end{array}$$

It is a colourless, mobile liquid, boiling at 84° C., and was first prepared in 1795.

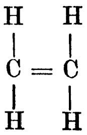
Now when phosphorus pentachloride acts upon aldehyde, C_2H_4O, it substitutes two chlorine atoms for one oxygen atom, and gives a dichloro ethane, $C_2H_4Cl_2$. This body is also formed by the action of chlorine on ethyl chloride, C_2H_5Cl. It boils at 57° C. instead of 80° C. and differs from ethylene dichloride in its chemical properties. The explanation given is that in this case the two chlorine atoms are attached to the same carbon atom, while in the former case they are attached to different carbon atoms.

The second body is called *ethylidene chloride*, and is represented by the formula $CH_3 - CHCl_2$.

The existence of these two bodies with the same molecular formula but with different properties is another illustration of *isomerism*, and of the extraordinary fertility of the hypothesis of valency applied to the question of molecular structure and structural formulae.

291. Unsaturated Hydrocarbons.—The characteristic differences between the properties of ethylene and ethane are accompanied by a difference in composition. Ethylene contains two atoms of hydrogen per molecule less than ethane, and its molecule is able to take up two other monovalent atoms or groups, but no more, in the place of the missing hydrogen atoms. The difference is best summarised by considering that the two carbon atoms of the ethylene molecule are trivalent, so that they can take up two other monovalent atoms or groups and thus become tetravalent. On this account ethylene is called an *unsaturated* hydrocarbon.

A convention has been almost universally adopted to express the existence of a pair of trivalent carbon atoms, viz., a double bond, so that ethylene may be given the structural formulae



$$\begin{array}{ccc} H & & H \\ | & & | \\ C & = & C \\ | & & | \\ H & & H \end{array} \qquad \text{or} \qquad H_2C = CH_2$$

Unsaturated carbon atoms appear to be able to exist only in pairs, so that the compound CH_2 cannot be prepared from methyl chloride, since the unsaturated carbon atoms immediately pair off and form ethylene, $CH_2 = CH_2$.

Just as in the case of methane and ethane, a whole series of homologues of ethylene exists, forming the *olefine series.* The characteristic property of this series is the formation of addition compounds by union with two monovalent atoms or groups.

292. Acetylene.—To proceed with our investigations, when we try the effect of removing chlorine or bromine from the molecules of ethylene dichloride or dibromide by the action of a caustic alkali in alcoholic solution, we find that a new gas is produced with the characteristic smell of a Bunsen burner burning back. The gas is found to be represented by the molecular formula C_2H_2 and is called *acetylene.*

The same gas is formed, mixed with marsh gas, when electric sparks are passed between carbon poles in an atmosphere of hydrogen or of marsh gas, and the product contains 10 per cent. of acetylene and 2·5 to 3 per cent. of marsh gas in excess of hydrogen. A more convenient method of preparing the gas is by the action of water on calcium carbide, CaC_2, a product of heating quicklime with carbon in the electric furnace.

Exp. 358.—Take a pneumatic trough of water and drop in a lump of calcium carbide. Cover the lump with an inverted cylinder of water and collect the gas. Notice the colour, taste, and smell of the gas. Test it with a light; it burns with a bright smoky flame. Pour into one cylinder some cuprous ammonium chloride solution* and add a few drops of liquor ammonia; a bright red precipitate is immediately formed.

293. Properties of Acetylene.—Acetylene is a colourless gas with a characteristic taste and smell. It boils at 0° C. under a pressure of 21·5 atmospheres. It dissolves in its own volume of water. It unites directly with chlorine, bromine, hydrochloric acid, hydrobromic acid, and sulphuric acid to form addition products by combining with two or four monovalent atoms or groups; of these products $C_2H_2Br_4$, *acetylene tetrabromide*, is the most often used. Acetylene burns in air with a very luminous flame and explodes when mixed with air or oxygen, and occasionally it detonates violently. (Hence it is dangerous to attempt to explode the mixture.) If forms a red compound with cuprous chloride, *cuprous acetilide*, Cu_2C_2, which is decomposed by the action of acids, acetylene being again set free. Acetylene is formed when hydrocarbons burn in an insufficient supply of air or oxygen.

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* Made by boiling copper oxide with hydrochloric acid and copper filings. Pour the product into water, allow the white precipitate to settle, pour off most of the liquid and add ammonium chloride until the precipitate dissolves.

Exp. 359.—Take a dry cylinder, invert it over a Bunsen burner burning at the bottom. In a few seconds nearly close the cylinder with a glass plate and pour in a small quantity of cuprous ammonium chloride solution. Shake up well and then pour one or two drops of ammonia solution down one side of the cylinder; a red precipitate is formed, showing the presence of acetylene in the products of combustion.

Acetylene is a poisonous gas combining, like carbon monoxide and nitric oxide, with the haemoglobin of the blood.

The properties and composition of this gas are generally summarised in the symmetrical structural formula

$$HC \equiv CH,$$

which contains a pair of carbon atoms united by a triple bond.

Acetylene like ethylene is the first member of a series of unsaturated homologues, the *acetylene series.*

294. Benzene.—Since the carbon atom is only tetravalent it is useless to proceed at present in the direction of removing more hydrogen atoms from its simpler compounds, so we return to the liquid product of the distillation of wood or coal, the *tar.*

In the fractional distillation of coal tar a rough separation of the distillate is made by collecting it in water. Part floats, the light coal tar naphtha, and when this is redistilled a considerable fraction is collected in the form of a liquid, which boils between 80° and 82° C. When lit it burns, forming carbon dioxide and water and nothing else (except carbon in the form of soot). Its percentage composition and molecular weight are represented by the formula C_6H_6 and it is called *benzene* or *benzol*. A similar method can be used for separating the constituents of wood tar.

295. Reactions of Benzene.—Chlorine acts fairly readily on benzene in the cold, and more readily in presence of iodine. Fumes of hydrochloric acid are given off, and the product obtained contains chlorine atoms substituted for hydrogen atoms. Now the formula suggests that the carbon atoms cannot all be tetravalent, or that some of them must be connected by double bonds, *i.e.* that the carbon atoms are unsaturated, and it is hardly to be expected that an unsaturated body of the character of ethylene or acetylene would form substitution instead of addition products. In sunlight, however, addition of chlorine does take place, and the addition is limited to six atoms forming $C_6H_6Cl_6$, called *benzene hexachloride*. This body easily splits off hydrochloric acid on heating, forming $C_6H_3Cl_3$, called *trichlorobenzene*.

Hydrochloric acid has no action on benzene, which thus presents another contrast with ethylene.

Hydriodic acid has no action on benzene, unless heated with it in a sealed tube, when two, four, or six hydrogen atoms may be added, forming bodies of the formulae C_6H_8, C_6H_{10}, and C_6H_{12}. The strongest hydriodic acid in the same circumstances can even add eight hydrogen atoms, but the product is now identical with a hexane, C_6H_{14}, a characteristic paraffin, and it has lost its characteristic benzene properties.

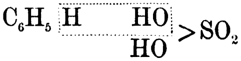
296. Action of Sulphuric and Nitric Acids on Benzene.—Nitric acid has a remarkable and characteristic action on benzene.

Exp. 360.—Take a small flask and put into it a mixture of 35 c.c. of strong nitric acid with 40 c.c. of concentrated sulphuric acid. Drop into the mixture a few c.c. (not more than 20 c.c.) of benzene, taking great care to add it gradually, to keep it well shaken, and to keep the flask cool; when all the benzene has been added warm to about 60° C. The benzene becomes yellow and gives off a smell of bitter almonds. Pour the mixture into water, separate the yellow oil, dry it by calcium chloride and distil it (Fig. 90). Any unchanged benzene distils over first, but the boiling point of the mixture rises and a fraction is collected boiling at about 210° C.

The product is a yellow liquid with a characteristic smell of almonds, and boiling at 210° C. Its analysis suggests the formula $C_6H_5NO_2$, and its molecular weight agrees with this formula. It is called *nitro-benzene*, the group $—NO_2$, which replaces one atom of hydrogen in the benzene, being called the *nitro group*. In this case it appears that the substitution of a nitro group in benzene is attended by a reduction of the nitric acid to the nitrous state, the hydrogen of the benzene combining with the hydroxyl of the acid to form water. Thus the greater part of the reaction may be represented by the equation

$$C_6H_6 + NO_2OH = C_6H_5NO_2 + H_2O.$$

Sulphuric acid has a similar reaction when heated with benzene for some time. A body of the formula $C_6H_5 . SO_3H$ *benzene sulphonic acid* or *sulphobenzene* is formed, which contains one atom of hydrogen replaceable by the metal of a base. It is an acid formed by reducing sulphuric acid by the hydrogen of benzene, water being formed as well, as suggested by the formulae



$$C_6H_5\begin{matrix}\boxed{H \quad HO} \\ HO\end{matrix} > SO_2$$

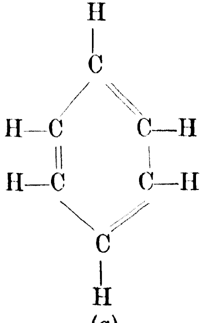
or expressed in the form of an equation

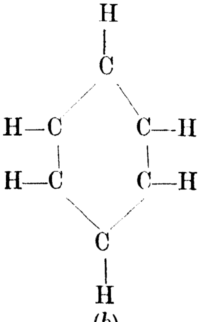
$$C_6H_6 + SO_2(OH)_2 = C_6H_5 . SO_3H + H_2O.$$

Weak solutions of alkalies and acids have no action on benzene, nor have metals in the cold. Oxidising agents form bodies with two or more hydrogen atoms replaced by oxygen.

297. Structural Formula of Benzene.—In the case of benzene, then, we have to explain these facts :—(i) From its formula we should expect it to form only addition compounds, yet it forms substitution compounds in its reactions with chlorine, nitric acid, and sulphuric acid. (ii) From its formula we should expect to be able to add eight hydrogen atoms or chlorine atoms in order to make all the carbon atoms tetravalent, yet we find it is difficult to add more than six such atoms and with the addition of two more we get an abrupt change of properties to those of a paraffin. (iii) The six carbon atoms always keep together as long as the properties are characteristic of benzene. (iv) The six hydrogen atoms seem to be symmetrically situated in the molecule, since we can prepare six monochlorobenzenes in which each hydrogen atom is substituted in turn, and they are all identically the same. The most probable induction from these facts is that the carbon atoms are symmetrically connected.

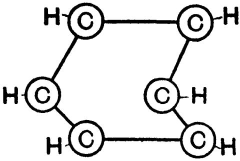
Several structural formulae have been suggested to represent these facts, but practically only two are in use. The first, suggested by Kekulé, represents all the carbons arranged in the form of a hexagon in one plane. This formula is set out in two ways, showing the carbon atoms as tetravalent and connected alternately by double and single bonds (*a*), and alternatively (*b*) showing all the carbon atoms symmetrical and trivalent.


(*a*)


(*b*)

The arrangement in (*a*) does suggest the possibility of adding hydrogen atoms in three pairs, by breaking a double bond in each case, and both formulae indicate that hexane can be formed only by breaking the ring in order to add four pairs or eight hydrogen atoms.

The most recent formula represents the hydrogen atoms as arranged in three pairs lying in more than one plane, and forming more or less a triangular prism.



It would be well to remind ourselves that a *structural formula* is principally a convenient shorthand for embodying facts and reactions, and may not represent any fixed arrangement of the atoms within the molecule.

Hydrocarbons which we assume to be built up on the plan of benzene with a closed chain of carbon atoms are said to have a *cyclo structure*, in distinction to those which have an *open chain structure*.

298. Other Methods of preparing Benzene.—Two other methods of preparing benzene should be mentioned.

Exp. 361.—Take a few grams of sodium benzoate and heat it in a test-tube with excess of soda lime. (Fig. 95.)

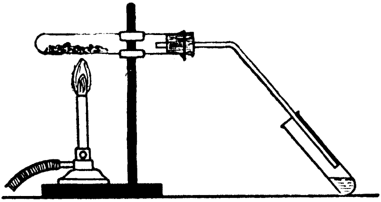


Fig. 95.

Drops of a liquid are formed, which have the properties of benzene.

The reaction between a benzoate and an alkali may be expressed by means of an equation which represents part of the reaction, and indicates the similarity between this method of preparation and that of preparing the paraffins.

$$\underset{\text{Sodium benzoate}}{C_7H_5O_2Na} + NaOH = Na_2CO_3 + C_6H_6$$

The second method is to pass acetylene through a red-hot tube. The molecules of acetylene join together and form bodies of the formulae C_4H_4, C_6H_6, and C_8H_8.

The C_6H_6 is benzene, and it will be noticed that its percentage composition is the same as that of acetylene, though its molecular weight is three times as great. Now, when we have two bodies with the same percentage composition, but different molecular weights, the body with the higher molecular weight is said to be a *polymer* of the other. Sometimes the polymer has properties which are similar to those of the original, but sometimes, as in this case, the properties are very different. The phenomenon is termed *polymerism.*

299. Toluene.—Just as we can substitute hydrogen atoms in open chain hydrocarbons by hydrocarbon groups, so we can do the same in the case of benzene. The resulting bodies combine the properties of both nucleus and substituted groups.

The first of these derivatives of benzene, formed by replacing one hydrogen atom by a methyl group, is also found in coal tar, and is called *toluene*, $C_6H_5CH_3$. It is obtained from the fraction boiling between 110° and 112° C., and has a boiling point of 110° C.

Toluene is poisonous to the amoeboid animalculae living in the soil, and has been used in soil sterilisation.

CHAPTER XXV.

ALCOHOLS, ETHERS, GLYCERIN.

300. Oxidation of the Hydrocarbons.—In inorganic chemistry we began by considering the products of oxidation of common bodies, and we discovered that there are elements and compounds, and that the elements form oxides with contrasting characters which we call basic and acid oxides.

If we pursue this method in organic chemistry we find that it does not lead to much result. By trying to oxidise the hydrocarbons we generally get only carbon dioxide and water, though in certain circumstances, *i.e.* an insufficient supply of air or oxygen, we obtain hydrocarbons with less hydrogen than the originals, *e.g.* acetylene from marsh gas.

On the other hand when we act on the hydrocarbons with chlorine we form substitution derivatives which resemble the chlorides of the elements, if we consider the organic radicles, methyl — CH_3 and ethyl — C_2H_5 respectively, as playing the part of elements. Thus CH_3Cl resembles KCl.

If we take this point of view we should expect to be able to obtain oxides or hydroxides of the radicles by the general method of preparing bases, *i.e.* by the action of caustic soda on the salt. When this experiment is tried, that is when a solution of methyl chloride, or when methyl iodide is heated with caustic soda, in addition to the ethylene already noted, a liquid is formed which mixes with water, but may be partly separated from it by distillation, as it boils at 66° C.

Analysis gives the formula CH_4O, which agrees with the inference that the hydroxide CH_3OH should be formed, as suggested in the equation

$$CH_3Cl + NaOH = CH_3OH + NaCl.$$

If this is confirmed we can consider the hydrocarbons as *hydrides* of the organic radicles of which we have now been able to prepare a chloride and a hydroxide in the case of methyl.

$$\begin{aligned} CH_3Cl &= \text{methyl chloride,} \\ CH_3OH &= \text{methyl hydroxide,} \\ CH_3H &= \text{methyl hydride,} \end{aligned}$$

so that we have been able to produce oxidation of our hydrocarbons, not directly, but by the stratagem of replacing hydrogen by chlorine and then chlorine by hydroxyl (OH).

301. Alcohol.—When prepared in this way the hydroxides are found to be identical with bodies prepared in many other ways, *e.g.* by the action of caustic soda on essential oils, the fermentation of sugar solutions, and the distillation of organic compounds.

Spirit of wine or common *alcohol* is the most familiar of the class and may easily be investigated.

Exp. 362.—Take a large flask and place it in some solution of grape sugar. Place some yeast in the flask and shake it well; put the flask in a warm place and allow it to stand for a few days. Observe the frothing and prove that it is due to the formation of carbon dioxide. After a time, fit the flask with a cork and bent tube connected with a condenser (Fig. 96), and distil off a few c.c. of the liquid. Apply a light to a few drops; the liquid burns. Mix a few drops with water, iodine, and caustic soda solution; the characteristic smell of iodoform is noticed.

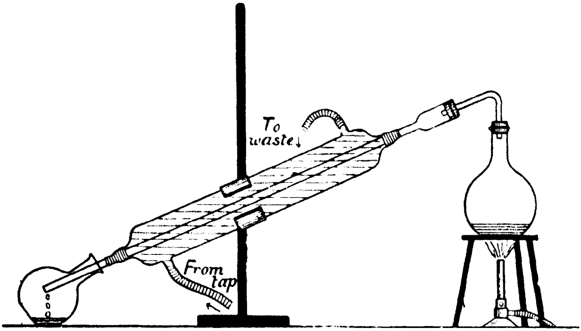


Fig. 96.

By the action of yeast on grape sugar solutions alcohol is formed. The yeast as seen under a microscope is composed of small rounded plant cells belonging to the class of the Fungi. This plant *Saccharomyces* (*Torula*) *cerevisiae*, as well as several others, when immersed in water obtains part of the energy required for building up its cell substance from a splitting up of sugar into carbon dioxide and alcohol. The equation

$$C_6H_{12}O_6 = 2\,C_2H_6O + 2\,CO_2$$

accounts for 95 per cent. of the changed sugar, about 3 per cent. appearing as glycerin, and ·5 per cent. as succinic acid. The other 1·5 per cent. is apparently oxidised further.

[It may be noted here that in presence of more oxygen than can be obtained from its solution in water, sugar is almost completely oxidised by yeast to carbon dioxide and water, so that in the manufacture of bread only a very small amount of alcohol is formed.]

The alcohol prepared by distillation is naturally wet, and it is dried by standing over and distillation from freshly prepared quicklime. This removes nearly all the water, and the final traces can be removed when required by sodium.

302. Properties of Alcohol.—Pure or absolute alcohol is a colourless liquid with a characteristic burning taste and smell. It burns when lighted. It boils at 78·3° C., freezes at − 130° C., and has a specific gravity of ·79. It mixes in all proportions with water and with ether, and it readily absorbs water vapour from the air. On mixing with water there is a contraction of volume, 52 c.c. of alcohol and 48 c.c. of water making only 96·4 c.c. of the mixture. Its solution in water will not allow gunpowder moistened with it to take fire when a light is applied unless it contains at least 49·3 per cent. by weight of spirit. A solution containing this percentage of alcohol is consequently known as *proof spirit.*

Alcohol dissolves many substances insoluble in water, *e.g.* resins, etc., and so is much used in manufactures. To prevent the drinking of this alcohol, which does not pay duty, it is *methylated* by adding 10 per cent. of crude wood spirit and as much paraffin as it will dissolve. On the Continent, bone oil is often added for the same purpose.

303. Chemical Reactions of Alcohol.—Chlorine acts upon alcohol, substituting three hydrogen atoms by three chlorine atoms and at the same time removing two more hydrogen atoms by oxidation. A body of the formula C_2Cl_3HO is formed, which is called *chloral* and which crystallises from water forming *chloral hydrate*, $C_2Cl_3H_3O_2$.

Hydrochloric and hydrobromic acids act on alcohol, substituting chlorine or bromine for one oxygen and one hydrogen atom and forming ethyl chloride and ethyl bromide respectively. These reactions suggest the basic character of alcohol, thus

$$C_2H_5OH + HCl = C_2H_5Cl + H_2O.$$

Hydriodic acid also replaces hydroxyl by hydrogen, forming an iodide as an intermediate product, but the hydriodic acid attacks this iodide forming free iodine and ethane ; this may be put in equation form, thus

$$C_2H_5OH + HI = C_2H_5I + H_2O,$$
$$C_2H_5I \quad + HI = C_2H_6 + I_2.$$

Sulphuric acid combines with alcohol, forming an acid sulphate, *ethyl hydrogen sulphate*, thus

$$C_2H_5OH + H_2SO_4 = C_2H_5 \,.\, HSO_4 + H_2O.$$

Oxidising agents, *e.g.* chromic acid or alkaline permanganate solution, oxidise alcohol very readily to *aldehyde*.

Exp. 363.—Take two or three drops of alcohol in a test-tube, add potassium bichromate solution and sulphuric acid, and warm the mixture.

The chromic acid turns green from reduction, and a new and characteristic fruity smell, due to aldehyde, is noticed.

Since nitric acid is an oxidising agent as well as an acid, its reaction with alcohol is very complicated, part of the alcohol being oxidised and part of the nitric acid being reduced. The reduced nitrous acid combines with the alcohol to form *ethyl nitrite*, $C_2H\,NO_2$, as well as *ethyl nitrate*, $C_2H_5NO_3$.

Alcohol thus has the properties of an ordinary base and combines with acids, forming salts and water.

Sodium dissolves readily in alcohol, replacing hydrogen and forming a body, sodium alcoholate or *sodium ethylate*, represented by the formula C_2H_5ONa.

A most important reaction is that between alcohol and phosphorus pentachloride which acts readily on alcohol, substituting one chlorine atom for one oxygen and one hydrogen atom, and forming ordinary ethyl chloride, C_2H_5Cl. These two atoms must hence be arranged in the molecule in the form of a group (— O — H), a *hydroxyl group*. The reaction is so characteristic that it is used in the preparation of the haloid derivatives of the paraffins.

304. Structural Formula of Alcohol.—In making a formula to represent the structure of alcohol, the following points must be considered:—

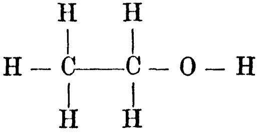
(i) The percentage composition and the molecular weight indicate the formula C_2H_6O.

(ii) Phosphorus pentachloride by substituting one O and one H atom by one Cl atom shows that the hydroxyl group (— OH) is present.

(iii) Chlorine replaces 3 H atoms by 3 Cl atoms, showing that 3 H atoms are differently arranged from the other three.

(iv) Alcohol is prepared from ethyl chloride by substitution of the OH group for the Cl atom.

The formula can be arranged in only one way to agree with these reactions, the valencies of the atoms, and the presence of the hydroxyl group. The arrangement is



$$\begin{array}{ccccccccc} & & H & & H & & & & \\ & & | & & | & & & & \\ H & - & C & — & C & - & O & - & H \\ & & | & & | & & & & \\ & & H & & H & & & & \end{array}$$

which represents it as ethyl hydroxide. This is taken as the formula of alcohol.

305. Methyl Alcohol.—We may now return to the first alcohol made by the action of caustic soda solution on methyl chloride, *i.e.* *methyl alcohol*. This was first prepared and examined by Robert Boyle in 1661.

It is commonly prepared by the distillation of wood. The distillate, which is acid, is neutralised by lime and again distilled. The fraction boiling about 60°—70° C. contains the methyl alcohol. This *wood spirit* is very difficult to purify. Methyl alcohol is also prepared by distilling wintergreen oil with caustic soda solution. Sodium salicylate is formed at the same time.

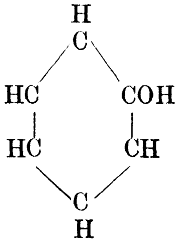
$$\underset{\text{Wintergreen oil}}{C_8H_8O_3} + NaOH = \underset{\text{Sodium salicylate}}{Na\,.\,C_7H_5O_3} + CH_3OH.$$

Methyl alcohol is a colourless liquid boiling at 66° C. and of specific gravity ·8. Its properties are so similar to those of ethyl alcohol that it is not necessary to repeat them. It differs, however, when pure, in one important particular, viz. it does not form chloroform or iodoform by the reaction of bleaching powder or iodine and caustic soda solution respectively.

306. General Methods of Preparing Alcohols.—Some other alcohols are common bodies, *e.g.* *fusel oil*, $C_5H_{11}OH$, and it is possible to make many alcohols by *general methods*, *i.e.* from hydrocarbons, etc. The most general method is the substitution of chlorine for hydrogen in the hydrocarbon, followed by the substitution of hydroxyl for chlorine by means of caustic soda, or better, by freshly prepared silver hydroxide. This method gives a poor yield owing to the formation of ethylenes.

307. Phenol.—If we attempt to prepare a hydroxide or alcohol from benzene by the action of caustic soda on monochlorobenzene, we find that no action takes place. If, however, we take the product of the action of sulphuric acid on benzene, benzene sulphonic acid, $C_6H_5SO_3H$, and treat that with caustic potash, first in solution to form a potassium salt, potassium benzene sulphonate, $C_6H_5SO_3K$, and then by fusing the salt with caustic potash in a silver basin, we find that a change has taken place.

The fused mass is soluble in water, and on addition of dilute acid deposits a liquid which sinks to the bottom and may be separated. The liquid has a characteristic smell of carbolic acid, and blisters the skin. Its percentage composition and molecular weight are represented by the formula C_6H_6O, and it is called *phenol*. Phosphorus pentachloride reacts with it and substitutes hydroxyl by chlorine, so that its formula must be represented by C_6H_5OH, or structurally



The mode of formation may be represented by the equation

$$C_6H_5 . SO_3K + KOH = C_6H_5OH + K_2SO_3.$$

The method is general for benzene compounds, and applies to the insertion of any number of hydroxyl groups.

308. Preparation and Properties of Phenol.—Phenol is generally prepared from coal tar. The fraction of the distillate boiling between 150°—200° C. is taken, mixed with a solution of caustic soda, and the heavy solution separated off. The solution is mixed with dilute sulphuric acid and the resulting oily liquid redistilled. The portion boiling about 180°—190° C. is again separated and is phenol, or carbolic acid, so called because it combines with alkalies to form soluble compounds resembling salts. The lime salt has been used in estimating quicklime, see Art. 214.

Phenol is generally liquid, but when freed from water may be crystallised as a solid melting at 42° C. and boiling at 182° C. It is colourless when first prepared, but soon reddens on exposure to the air. It dissolves in fifteen parts of water, in alcohol, and in ether.

Exp. 364.—To a solution of phenol in water add some ferric chloride solution to which alkali has been added until nearly neutral. A violet colour is seen. To some more of the solution add a drop of bromine. A yellowish precipitate is at once formed. Dip a pine splinter into phenol and then dip it into hydrochloric acid; it soon turns green. Add a solution of caustic soda to some phenol; it now dissolves in water.

A characteristic property of phenol is that it acts as a germicide in strong solutions, and better in the liquid state ; in dilute solution, on the other hand, it has very little action.

309. Ether.—Since the properties of alcohols are similar to those of metallic bases we might expect that they would form oxides on heating, just as most bases do ; but this is seldom the case, so that the alcohols resemble the caustic alkalies in this respect. It is, however, easy to remove water in presence of a dehydrating agent; in the case of ethyl alcohol, sulphuric acid is used.

Exp. 365.—Fit up a flask with a condenser, dropping funnel and thermometer reaching nearly to the bottom of the flask. In the flask place a mixture of about equal volumes of sulphuric acid

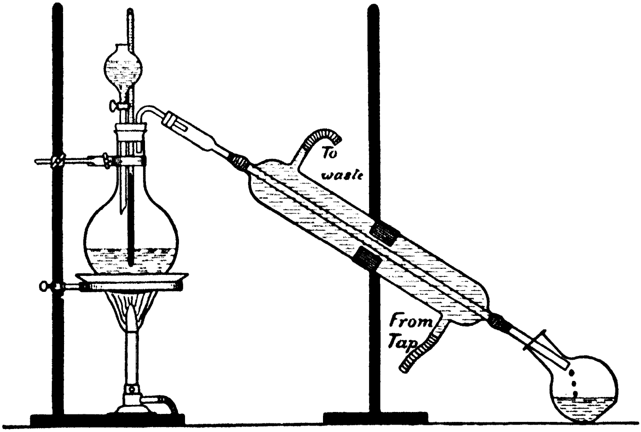


Fig. 97.

and alcohol, and heat it on a sand bath or gauze to about 140° C. Fill the dropping tube with a mixture of alcohol and sulphuric acid and allow it to trickle in from time to time. A volatile liquid comes over, with a characteristic smell of ether.

310. Properties of Ether.—Ether is a volatile, mobile, colourless liquid of specific gravity ·72, boiling at 35° C. and solidifying at $-129°$ C. Its percentage composition and molecular weight are represented by the formula $C_4H_{10}O$. When ether is rapidly volatilised, the heat which is rendered latent in the vapour is supplied by any bodies with which it is in contact and they become very cold, so much so that an ether spray is largely used to produce local cooling.

Ether acts as a solvent and is able to extract many bodies from their solutions in water. It has also a valuable anaesthetic action. Ether burns in air and explodes with oxygen; care must always be taken to evaporate ether only on a water bath and without a flame near it.

Hydriodic and sulphuric acids act upon ether, splitting it up into a mixture of ethyl alcohol and ethyl iodide or ethyl hydrogen sulphate, respectively.

Phosphorus pentachloride acts upon ether when they are heated together, substituting two chlorine atoms for one oxygen atom and splitting the molecule up at the same time into ethyl chloride only. In order to explain these reactions we must assume that ether is an oxide of ethyl, $(C_2H_5)_2O$, corresponding to the hydroxide alcohol, C_2H_5OH, and bearing the same relation to it as the oxide of sodium, Na_2O, does to its hydroxide, NaOH.

311. The Reactions between Sulphuric Acid and Alcohol.—We can now explain the reactions between sulphuric acid and alcohol. When sulphuric acid is mixed with alcohol, the acid sulphate, ethyl hydrogen sulphate, $C_2H_5 . HSO_4$, is formed, and the water is removed by the acid.

$$C_2H_5OH + H_2SO_4 = C_2H_5 . HSO_4 + H_2O.$$

The acid sulphate when heated to 160° C. in presence of sulphuric acid splits up into ethylene and sulphuric acid, thus :—

$$C_2H_5 . HSO_4 = C_2H_4 + H_2SO_4.$$

But if there is an excess of alcohol and the temperature is kept below this, about 140° C., then the alcohol reacts with the acid sulphate, forming ether and sulphuric acid. The equation may be given thus :—

$$C_2H_5 \,.\, HSO_4 + C_2H_5OH = (C_2H_5)_2O + H_2SO_4.$$

Since the sulphuric acid is regenerated, the process is continuous so long as the sulphuric acid is strong enough to form the acid sulphate. It is hence called the *continuous etherification process*.

It may have been noticed that the formula $C_4H_{10}O$ could also be written to represent an alcohol, C_4H_9OH, *butyl alcohol*, as well as ethyl ether, $(C_2H_5)_2O$. It would appear from this that ethers may have the same percentage composition and molecular weight as alcohols, *i.e.* an ether and an alcohol may be isomeric compounds.

312. Polyacid Bases.—We have seen that the alcohols are hydroxides with oxides corresponding to them; they are *monacid* or *monad bases* derived from hydrocarbon radicles. We also find diacid or diad bases and triacid or triad bases among the alcohols, provided the hydroxyl groups are attached to different carbon atoms of the molecule.

It must be mentioned that there is some confusion of terms about this point, and the terms monatomic, diatomic, etc., and monohydric, dihydric, etc., alcohols are sometimes used instead of the *base* terminology given above. A little consideration will show the inadvisability of using the same adjective to express the number of atoms in a molecule and the number of hydroxyl groups in an alcoholic molecule.

313. Glycerin.—Only one of the polyacid bases need be discussed now, viz. *glycerin* or *glycerol*, discovered by Scheele in 1779.

In the manufacture of soap by the action of caustic soda on fats, the watery solution left after the separation of the soap may be evaporated down and distilled. After the water has evaporated, a sweetish liquid is left, which boils at about 290° C. Its molecular composition is represented by $C_3H_8O_3$, and it is *glycerin*. Glycerin is now prepared by the action of superheated steam on fats. Glycerin is a thick colourless syrup of specific gravity 1·27. It melts at 20° C. after being crystallised, and boils when pure at 290° C. It is very hygroscopic and is used in the manufacture of stamping inks, flexible glue, etc.

Exp. 366.—Apply a light to a little glycerin on a crucible lid; it does not burn. Heat the glycerin to 150° C. It now burns when lighted.

The reactions of glycerin are very complex. Hydrochloric acid forms salts, replacing one or two hydroxyl groups by chlorine. Nitric acid forms a nitrate, which contains three nitrate groups and is a tri-nitrate, $C_3H_5(NO_3)_3$. This body is nitro-glycerin or *trinitrin*, which explodes violently when its detonation is once started by a shock. Phosphorus pentachloride removes three hydroxyl groups and replaces them by three chlorine atoms, forming trichloropropane, $C_3H_5Cl_3$. These facts are best explained on the assumption that the three carbon atoms are directly united, and that there are three hydroxyl groups, one united with each carbon atom thus

$$CH_2(OH) - CH(OH) - CH_2(OH).$$

This formula is confirmed by synthesis.

As glycerin is an alcohol we might expect changes on dehydration; thus distillation with calcium chloride removes three molecules of water from two molecules of glycerin, forming *glycerin ether* $(C_3H_5)_2O_3$. Phosphoric anhydride and sodium hydrogen sulphate also remove water, forming *acroleïn*, C_3H_4O, a body with a characteristic smell of burnt fat.

CHAPTER XXVI.

ALDEHYDES: KETONES.

314. Aldehyde.—The oxidation of the hydrocarbons by the introduction of hydroxyl for hydrogen led to the alcohols, a distinct class of bodies, and alcohol readily reduces common oxidising agents. The oxidation is easily examined.

Exp. 367.—Take a flask fitted with a thistle funnel, and connected with a condenser, and place in it 20 gm. of potassium bichromate covered by 60 c.c. of water. Mix 20 c.c. of alcohol gradually and carefully with 15 c.c. of strong sulphuric acid. Cool the mixture, and run it into the flask through the thistle funnel. Be careful not to allow the temperature to rise, and not to run in the alcohol mixture too quickly. After all the mixture has been run in, warm gently. A liquid distils off and condenses. Redistil the distillate from a water bath at a temperature of 30° C., using a good condenser, and collect the portion boiling at about 20—22° C.

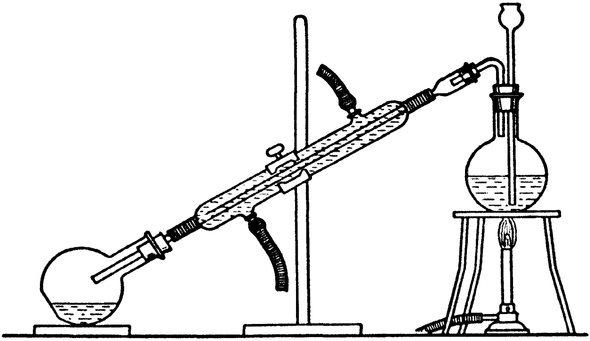


Fig. 98.

The distillate has different properties from alcohol, and its percentage composition and molecular weight are represented by the formula C_2H_4O. Its formula differs from that of the parent alcohol, C_2H_6O, by two hydrogen atoms and it was called *acetic aldehyde,* or more shortly, *aldehyde.*

315. Properties of Aldehyde.—Aldehyde is a colourless mobile liquid with a characteristic fruity smell and burning taste. It boils at 21° C. It is soluble in water, alcohol, and ether, and readily dissolves sulphur, phosphorus, iodine, and resins. Chlorine acts upon aldehyde forming various compounds; in presence of chalk and water it substitutes three chlorine atoms for three hydrogen atoms, and forms *chloral,* C_2HCl_3O, thus suggesting that three of the hydrogen atoms are similarly situated to each other and differently from the other one. Hydrochloric and sulphuric acids cause a curious and characteristic change. At ordinary .temperatures the effect of these acids is to raise the boiling point of the liquid, and at the same time its molecular weight becomes tripled. It is now represented by the formula $(C_2H_4O)_3$ as a polymer of aldehyde, and is called *paraldehyde.* If the aldehyde is at 0° C. the acids cause it to polymerise into a solid, *metaldehyde.*

Nitric acid, chromic acid, and other oxidising agents are readily reduced by aldehyde, more readily than by alcohol.

Exp. 368.—Take a solution of silver nitrate in a test-tube, add to it a few drops of ammonia solution until the precipitate at first formed redissolves. Then add a few drops of soda solution until the solution becomes slightly turbid. Add a few drops of aldehyde. The silver is reduced, more quickly on warming, in the form of a lustrous metallic lining to the tube, the *silver mirror.*

Add a few drops of aldehyde to some Fehling's solution (Exp. 383) of copper, and boil. A yellow precipitate of reduced cuprous oxide is seen.

This reduction of silver and copper is used as a test for aldehyde.

Sodium amalgam (Exp. 235), which displaces hydrogen from water, reduces aldehyde again to alcohol.

In presence of caustic alkalies aldehyde is readily resinified to *aldehyde resin,* another characteristic test.

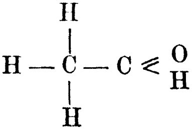
Exp. 369.—Boil a few drops of aldehyde in a test-tube with a strong solution of caustic soda. It turns yellow and then brown from the formation of aldehyde resin.

Another important test for aldehydes is used commercially.

Exp. 370.—To a very small quantity of magenta (fuchsine) crystals or solution gradually add sulphurous acid until the colour disappears (is *discharged*). Now add a drop of aldehyde solution.

The colour reappears, and this reappearance is a test for aldehyde.

316. Structural Formula of Aldehyde.—Phosphorus pentachloride substitutes two chlorine atoms for one oxygen atom without other change, indicating the absence of any single hydroxyl group and also that the carbon atoms are not joined by the oxygen atom. Hence if three hydrogen atoms are similarly situated (see Art. 315), if there is no hydroxyl group, and if the carbon atoms are connected, we arrange a formula for aldehyde thus :—



$$\mathrm{H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-C \lessgtr {}^{O}_{H}}$$

This formula does not readily indicate the connection between aldehyde and alcohol. Probably oxidation of alcohol to aldehyde takes place in a usual manner, viz. the oxidation of a hydrogen atom to a hydroxyl group, which may be represented thus :—

$$2\,\mathrm{CH_3CH_2OH} + \mathrm{O_2} = 2\,\mathrm{CH_3CH(OH)_2}.$$

Under ordinary conditions two hydroxyl groups attached to the same carbon atom readily split off water, in this case giving common aldehyde,

$$\mathrm{CH_3CH(OH)_2} = \mathrm{CH_3CHO} + \mathrm{H_2O}.$$

We can now understand why phosphorus pentachloride substitutes the oxygen atom by two chlorine atoms, since the oxygen atom represents what is left of two hydroxyl groups.

317. Reactions of Aldehyde with Acids and Bases.—Aldehyde with its two hydroxyl groups has the properties of a higher metallic oxide, and can unite with both a weak acid and a weak base; thus it combines (i) with ammonia forming a clear crystalline compound, *aldehyde ammonia*, and (ii) with hydrocyanic acid (see Art. 345) forming a hydroxy cyanide. Equations may be given,

(i) $CH_3CH(OH)_2 + NH_3 = CH_3CH(OH)NH_2 + H_2O$

(ii) $CH_3CH(OH)_2 + HCN = CH_3CH(OH)CN + H_2O$.

318. Formaldehyde.—Methyl alcohol can be oxidised to an aldehyde in the same way as ethyl alcohol and the aldehyde formed contains only one carbon atom, so that it is the aldehyde having the lowest possible carbon content. It is called *formaldehyde* or *methyl aldehyde*, and is represented by the formulae

$$H - CHO \quad \text{or} \quad H - CH(OH)_2.$$

This body is readily formed by the oxidation of methyl alcohol by free oxygen under the influence of platinum, but its special interest is connected with the probability that it is the first product of reduction of carbonic acid by the green plant, which may perhaps be represented by the equation

$$CO(OH)_2 + H_2O = HCH(OH)_2 + O_2$$

Its properties are similar to those of aldehyde.

Formaldehyde is sold in solution in water as *formalin*, and is a poisonous substance. It is used to prevent putrefaction, but should not be used in food, especially in milk.

Exp. 371.—Repeat the last three experiments, using a drop of formalin instead of aldehyde.

Also test a sample of milk by the magenta test to see that it is free from formalin.

319. Acetone. Ketones.—We have already noted (Art. 305) that methyl alcohol is formed in the distillation of wood, and it is prepared from the watery part of the distillate. Other substances are present in the watery distillate and can be separated by careful fractional distillation. Among these is a substance boiling at 56° C. and having the percentage composition and molecular weight represented by C_3H_6O.

This formula is the same as that of an aldehyde containing three carbon atoms and called propyl aldehyde, but the two substances have different properties; the one prepared from wood distillate is called *acetone.* Thus while propyl aldehyde boils at 48° C., acetone boils at 56° C., and while the aldehyde has the characteristic reactions described in the preceding paragraphs, acetone is only slowly oxidised and does not readily act as a reducing agent.

The differences in properties can be best summed up in the structural formulae assigned to the two bodies, the aldehyde being represented as containing the characteristic *aldehyde group* $-CHO$, thus:—

$$CH_3CH_2CHO$$

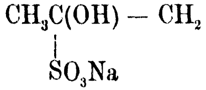
and the acetone as CH_3COCH_3.

The group $=C=O$ is called the *ketone group.* The carbon atom in this group is attached to two other carbon atoms, and the oxygen atom, which can be replaced by two chlorine atoms by the action of phosphorus pentachloride, represents, as in the aldehyde group, the remains of two hydroxyl groups from which water has been split off.

Ketones are isomeric with aldehydes of the same carbon content. The properties of the ketones are in many respects similar to those of the aldehydes but, as already noted, they do not easily act as reducing agents; oxidation involves the splitting up of the ketone molecule into two parts.

In reactions which do not involve the splitting up of the molecule the resemblance is marked; thus ketones and aldehydes both combine with ammonia to form solid compounds (see Art. 317).

Again, both ketones and aldehydes combine with sodium bisulphite to form a solid compound. Thus acetone forms the compound represented by the formula



$$CH_3\underset{\displaystyle SO_3Na}{\underset{|}{C}}(OH)-CH_2$$

in which one of the $-OH$ groups is reformed.

Both ketones and aldehydes can be prepared in the laboratory from salts of organic acids, as will be seen later in Art. 326.

CHAPTER XXVII.

ORGANIC ACIDS.

320. Oxidation of Alcohol.—Aldehydes have been seen to possess reducing properties, and the products of their oxidation may be collected and examined if we submit the aldehyde or the alcohol to the action of the oxidising agent for some time.

Exp. 372.—Take a half-litre flask, fitted with a cork and upright condenser so as to run the distillate back. Place in the flask about twenty gm. of potassium bichromate covered with dilute sulphuric acid (one in five). Warm by a water-bath and pour down the condenser a few c.c. of aldehyde or alcohol. The smell gradually changes to that of vinegar. Turn the condenser down and heat the flask. Collect the distillate coming over between 110° and 120° C. Test it with litmus, chalk, etc.

The distillate is acid and appears to be similar to vinegar, and to wood vinegar, from which it is generally prepared.

321. Preparation of Acetic Acid.—Vinegar is prepared from dilute spirit solutions by the action of *Bacterium aceti*, a fungus which oxidises the alcohol by means of the oxygen of the air while the solution is trickling over faggots.

The watery liquid obtained in the dry distillation of wood contains wood spirit and acetone, and is also sour from the presence of an acid.

From both of these products a pure acid is prepared by neutralisation with lime and crystallisation of the lime salt. The lime salt is purified by recrystallisation and distilled with hydrochloric or sulphuric acid. The vinegar acid distils over.

Exp. 373.—Take a small retort and place in it about five or ten gm. of calcium or sodium acetate. Cover this with strong sulphuric acid. Heat carefully and collect the product (Fig. 99). It is a pungent smelling liquid. Test it with litmus.

Whether prepared from aldehyde or vinegar, the properties of the body are the same. Its percentage composition and molecular weight are represented by the formula $C_2H_4O_2$, and it is called *acetic acid.*

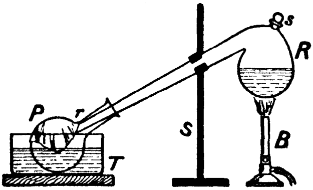


Fig. 99.

322. Properties of Acetic Acid.—Pure acetic acid is a colourless liquid of specific gravity 1·055. It blisters the skin, and has a characteristic pungent smell, which on dilution is like that of vinegar. It melts at 17° C. and boils at 118° C. It acts as a solvent for many bodies which are insoluble in water, *e.g.* sulphur and phosphorus.

Exp. 374.—Apply a light to some acetic acid in a basin. Heat the basin and apply a light again to the boiling acid.

Cold acetic acid does not burn, but its vapour burns at the boiling point.

Chlorine acts upon acetic acid by substitution only, and substitutes three chlorine atoms for three hydrogen atoms in succession, producing three different compounds, monochloroacetic, dichloroacetic, and trichloroacetic acids. No oxidation is noticed.

Hydrochloric acid, sulphuric acid, nitric acid, chromic acid, and oxidising agents generally have no action on acetic acid, but an alkaline solution of potassium permanganate is able to oxidise it (to oxalic acid). Phosphorus pentachloride acts on acetic acid, substituting one chlorine atom for hydroxyl, and forming *acetyl chloride,* $C_2H_3O \,.\, Cl$, a fuming liquid.

The most characteristic compounds of acetic acid are its salts, prepared by the direct reaction between the acid and bases or basic oxides. Acetic acid is a monobasic acid and contains only one atom of replaceable hydrogen per molecule. All its normal salts are soluble in water, but they are frequently decomposed by boiling water and give precipitates of a basic salt.

Exp. 375.—(i) Neutralise some acetic acid with soda and crystallise out the sodium acetate.

(ii) Dissolve litharge or lead carbonate in moderately strong acetic acid and crystallise out lead acetate (sugar of lead).

(iii) Add a solution of acetate of soda to ferric chloride. Neutralise and boil the solution.

A red solution of ferric acetate $Fe(C_2H_3O_2)_3$ is first formed, from which a brown precipitate of basic ferric acetate, $Fe(OH)_2C_2H_3O_2$ comes down on boiling. This precipitate is insoluble in water, and is used to remove iron from solutions containing phosphates.

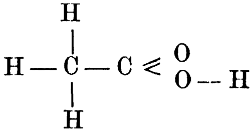
323. Formula of Acetic Acid.—We have now sufficient data to decide on a structural formula for acetic acid, which must embody the facts :—

(*a*) One atom of hydrogen is replaceable by metals and one hydroxyl group by chlorine by the action of phosphorus pentachloride.

(*b*) Three hydrogen atoms are different from the other one and can be substituted by chlorine without destroying the acid characters of the body.

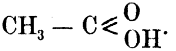
(*c*) The acid is prepared from aldehyde by oxidation, one hydrogen atom being replaced by a hydroxyl group.

Considering these facts in the light of the valencies of the atoms concerned, the formula must be arranged like this :—



$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-C\leqslant\begin{matrix}O\\O-H\end{matrix}$$

and taking (*a*), (*b*), and (*c*) in order, sodium acetate is represented by $CH_3C{<}\begin{matrix}O\\ONa\end{matrix}$, acetyl chloride by $CH_3C{<}\begin{matrix}O\\Cl\end{matrix}$, and the three chloroacetic acids by $CH_2ClCOOH$, $CHCl_2COOH$, and CCl_3COOH respectively.

The process of oxidation is evidently only a continuation of the oxidation of alcohol to aldehyde by the conversion of a hydrogen atom into a hydroxyl group; thus alcohol, CH_3CH_2OH, is oxidised to aldehyde, $CH_3CH(OH)_2$, which is oxidised further to acetic acid, $CH_3C(OH)_3$. Just as aldehyde cannot keep its two hydroxyl groups attached to one carbon atom, so acetic acid cannot do so and water is split off, leaving  $CH_3 - C \lessgtr {}^{O}_{OH}$. This monovalent group of atoms (—COOH) is termed the *carboxyl group*, and so general is the presence of this group in organic acids that they are generally defined by its presence in preference to the possession of the properties selected for defining inorganic acids.

324. Synthesis of Organic Acids.—Additional weight is given to the formula for acetic acid by a method of building it up from marsh gas.

Methyl chloride or iodide is converted into methyl cyanide by the action of an alcoholic solution of potassium cyanide. The resulting methyl cyanide contains two atoms of carbon, so we have added one carbon atom to the methyl group. When the cyanide is boiled with dilute acids it splits up into ammonia which combines with the acid, and acetic acid, thus,

$$\begin{aligned} CH_3CN + 3\,H_2O + HCl &= CH_3C(OH)_3 + NH_4Cl \\ &= CH_3COOH + NH_4Cl + H_2O. \end{aligned}$$

This is a most important general method of synthesising organic acids by the addition of carbon atoms, one at a time.

325. Formic Acid.—When we start to oxidise methyl alcohol, HCH_2OH, or methyl aldehyde, HCHO, we prepare at once an acid with the molecular composition represented by the formula, HCOOH, and called *formic acid* from its identity with an acid first prepared by distilling red ants. The method of preparing acids by oxidising alcohols is a general method.

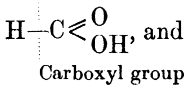
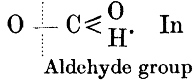
Formic acid is also prepared by distilling oxalic acid with glycerin, but the reaction is complicated.

Formic acid is a colourless liquid of specific gravity 1·22, boiling at 99·9° C. and freezing at 8·6° C. Its reactions are very similar to those of acetic acid, and all its salts are soluble. As it has only one carbon atom it is the lowest organic acid and cannot very readily form substitution derivatives.

It has, however, two very important differences from acetic acid; (*a*) when boiled with sulphuric acid it forms carbon monoxide, (*b*) it is very readily oxidised even by weak oxidising agents.

Exp. 376.—Take a test-tube and pour into it about 1 c.c. of formic acid and 5 or 10 c.c. of sulphuric acid, and heat. Apply a light to the mouth of the tube. The gas given off burns with a characteristic blue flame forming carbon dioxide, so that it is carbon monoxide.

Take a solution of silver nitrate, add to it ammonia and soda, as in Exp. 368, and add formic acid and warm. A silver mirror forms. Take a solution of mercuric chloride, add formic acid and boil. The mercuric chloride is reduced to mercurous chloride.

This difference between the two acids is best explained after an inspection of the formula HCOOH, which can be arranged in two ways: (i) as an acid HCOOH or  $\mathrm{H}\,\vdots\!-\underset{\text{Carboxyl group}}{\mathrm{C}\!<^{\mathrm{O}}_{\mathrm{OH}}}$, and (ii) as an aldehyde HO — CHO or  $\mathrm{H}-\mathrm{O}\,\vdots\!-\underset{\text{Aldehyde group}}{\mathrm{C}\!<^{\mathrm{O}}_{\mathrm{H}}}$. In the latter case the formula is written as an aldehyde of hydroxyl which oxidises very readily to carbonic acid.

326. Reactions of the Organic Acids.—One important reaction of the acids has been already used. When heated with excess of soda lime the carboxyl group splits up, part being retained by the hydrocarbon formed from the residue of the acid, and part by the base in the form of carbonate, so that from an acid we can obtain a hydrocarbon with one carbon atom fewer. We can express the reaction generally by an equation using the symbol C_nH_{2n+2} to represent a paraffin.

$$C_nH_{2n+1}COONa + NaOH = C_nH_{2n+2} + Na_2CO_3.$$

When sodium formate is heated with soda lime, $n = 0$, and hydrogen is formed.

Two other important reactions may be noted; (i) heating the calcium salt of the acid alone, (ii) heating the calcium salt of the acid with calcium formate. The first reaction results in the formation of a derivative of the acid in which a hydrocarbon radicle takes the place of the hydroxyl in the carboxyl group, forming a *ketone*. In the case of calcium acetate an equation which represents part of the reaction, viz. the formation of the ketone, *acetone*, is

$$\underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} = \underset{\text{Acetone}}{CH_3COCH_3} + CaCO_3.$$

When calcium formate is used the hydrogen of the formate enters the carboxyl group in place of the hydroxyl group, thus causing a reduction of the acid to aldehyde. We may represent this part of the reaction, in the case of heating a mixture of calcium acetate and formate, by an equation,

$$\underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} + \underset{\text{Calcium formate}}{(HCOO)_2Ca} = \underset{\text{Aldehyde}}{2\ CH_3CHO} + 2\ CaCO_3.$$

The second reaction is of great interest, as it enables us to prepare aldehydes direct from acids containing the same number of carbon atoms.

Formic and acetic acids are the first two members of a whole series of acids derived from the paraffin series of hydrocarbons by the substitution of a carboxyl group for a hydrogen atom. Though there is a very large number of these acids we are principally concerned with the series in which all the carbon atoms are connected in a single chain. This series may be represented by the general formula $C_nH_{2n+1}COOH$, and is called the *acetic series*.

327. Benzoic Acid.—Many aromatic resins when heated with lime yield benzene, and when gum benzöin is heated by itself it forms a nearly colourless sublimate of fine needle-shaped crystals. These crystals when heated with lime yield benzene and calcium carbonate, so that they are a source of benzene. On analysis the crystals are found to have the molecular formula $C_7H_6O_2$. They melt at 121° C. and boil at 250° C. They are much more soluble in hot water than in cold; they dissolve readily in alkalies, and salts may be crystallised out from the solutions; the salts are much more soluble in water than the original substance.

When the crystals are treated with phosphorus pentachloride, hydroxyl is replaced by chlorine, forming a characteristic compound, resembling acetyl chloride. These reactions can be best explained by assuming that the crystals are an acid, *benzoic acid*, and that it contains the benzene ring, thus,

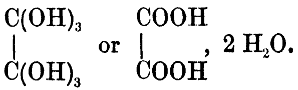
$$C_6H_5COOH.$$

328. Oxalic Acid.—When sorrel or rhubarb juice is evaporated a crystalline salt is formed, which is decomposed on heating, leaving potassium carbonate behind, and forming carbon monoxide and carbon dioxide. This suggests the presence of a salt of potassium and an organic acid, from which the acid may be prepared by precipitating the potassium salt as a lead salt by the addition of lead acetate, and precipitating the lead as lead sulphide by sulphuretted hydrogen.

Exp. 377.—Dissolve 10 or 15 gm. of salt of sorrel in water. Add a solution of lead acetate. Filter the precipitate and wash it well. Suspend the precipitate in water and pass in sulphuretted hydrogen. When all the lead is precipitated as lead sulphide, filter, and evaporate the filtrate; crystals separate out.

The crystals have the composition represented by the formula CH_3O_3, and are called *oxalic acid*, but as water is given off on heating and the substance left has much the same properties as the acid, the formula might be written CO_2H, H_2O. This substance is an acid, turning litmus red, and forming salts and water when it reacts with basic oxides and bases.

By solution methods we find that its molecular weight is represented by the double formula $C_2H_6O_6$ or $C_2H_2O_4, 2\,H_2O$, so that we can now make use of the fact that it has the same formula as carboxyl, a monovalent group, by writing the formula thus :—



$$\begin{array}{l} C(OH)_3 \\ | \\ C(OH)_3 \end{array} \text{ or } \begin{array}{l} COOH \\ | \\ COOH \end{array}, 2\,H_2O.$$

We satisfy both the properties of the acid, and the valencies of its atoms. This formula, showing the existence of two carboxyl groups in a molecule of the acid, suggests that the acid must be dibasic, and we find that this is the case ; oxalic acid forms two series of salts, the normal and the acid, represented in the case of potassium salts by the formulae

$K_2C_2O_4$, H_2O	and	KHC_2O_4 H_2O
Normal potassium oxalate		Acid potassium oxalate

This fact alone would make us infer that the doubled formula, $(CO_2H)_2$, 2 H_2O, must be used to represent the body.

329. Reactions of Oxalic Acid.—Chlorine, hydrochloric acid, and nitric acid have no action on oxalic acid, but it is readily oxidised to carbon dioxide and water by potassium permanganate or manganese dioxide and sulphuric acid.

Exp. 378.—Take a solution of oxalic acid, add a little dilute sulphuric acid, and warm it to 60° C. Run in a few c.c. of potassium permanganate solution or add a small quantity of solid manganese dioxide. The salt is decolorised or the oxide dissolved and bubbles of a gas are given off, which is proved to be carbon dioxide by lime water.

Heat decomposes oxalic acid ; first it splits off water at 100° C. and then decomposes further into a mixture of carbon monoxide and dioxide, and water. The action of strong sulphuric acid is similar and the oxalic acid splits up into a mixture of carbon monoxide and dioxide, the water being retained by the sulphuric acid.

Exp. 379.—Take a small flask fitted with thistle funnel and delivery tube. Place in the flask about 2 gm. of oxalic acid and cover with excess of strong sulphuric acid. Heat the flask and collect the gas formed over water saturated with carbon dioxide. Measure the volume collected, transfer it to caustic soda solution, and let it stand.

The gas is about half absorbed by the caustic soda, and the residue burns with a light blue flame, forming carbon dioxide. Hence the gases carbon dioxide and carbon monoxide are evolved in approximately equal volumes, so that the decomposition may be represented by the equation,

$$(COOH)_2, 2\,H_2O = CO_2 + CO + 3\,H_2O.$$

Oxalic acid forms a large series of salts, of which the most useful and characteristic are the normal and acid potassium oxalates already noticed, salt of lemon or sorrel, KHC_2O_4, $H_2C_2O_4$, 2 H_2O, and calcium oxalate, CaC_2O_4, which is insoluble in acetic acid, but soluble in hydrochloric acid.

330. Preparation of Oxalic Acid.—Oxalic acid is generally prepared from organic substances :—

(*a*) By the action of nitric acid on sugar.

Exp. 380.—Boil some sugar with nitric acid for some time in a small flask. Crystals separate out which should be recrystallised from water. The crystals are oxalic acid.

(*b*) By the action of hot caustic potash on sawdust or other forms of woody tissue. The mixture is fused in shallow iron pans, boiled out with water, acidified, and the oxalic acid crystallised out after the acidification.

331. Lactic Acid.—When milk goes sour, or when sugar is allowed to ferment in neutral solution under the action of *Bacillus lactis*, an organism which produces souring of milk, a characteristic acid, *lactic acid*, is formed.

If zinc oxide is used to keep the solution neutral, crusts of a crystalline zinc salt are formed. These crusts may be suspended in water and precipitated by means of sulphuretted hydrogen. On evaporation an oily liquid is left, with the percentage composition and molecular weight represented by $C_3H_6O_3$; this liquid is lactic acid. A similar body, *sarcolactic acid*, is found in muscular tissue.

Lactic acid acts on bases with the replacement of one atom of hydrogen by one atom of a monovalent metal, and when heated with lime it splits off carbon dioxide and forms alcohol. Probably then it is an acid with a carboxyl group, $C_2H_5O . COOH$. Hydrobromic acid substitutes one bromine atom for one hydroxyl group, forming a derivative of the corresponding acid of the acetic series with three carbon atoms, viz. : *monobromopropionic acid.* Hence there is probably a basic or alcoholic hydroxyl group in the molecule so that we may write it $C_2H_4(OH) . COOH$. This is confirmed by the fact that phosphorus pentachloride substitutes two hydroxyl groups by two chlorine atoms, so that lactic acid may be called a *hydroxy* or *oxy-propionic acid.*

When we come to draw up the possible formulae we find that there are two possible lactic acids, viz. :—

$$\underset{\beta}{CH_3}\underset{\alpha}{CH}(OH)COOH \quad \text{and} \quad \underset{\beta}{CH_2}(OH)\underset{\alpha}{CH_2}COOH$$

To remember which is which we adopt the plan of lettering the carbon atoms, starting from the group which gives the body its name ; in this case the carboxyl group gives the body the name of acid, so that the carbon atoms are lettered α, β, γ, etc., starting from the one attached to the carboxyl group.

Then the former acid becomes α-hydroxy propionic acid, and the latter β-hydroxy propionic acid.

We can prepare the two acids by different methods which leave no doubt as to the identity of the acid prepared ; thus to prepare the α-acid, we act upon aldehyde with hydrocyanic acid as mentioned in Art. 317.

$$CH_3CHO + HCN = CH_3CH(OH)CN.$$

The action of dilute acids converts this hydroxy cyanide into lactic acid and an ammonium salt. The methyl group can only be changed by substituting its hydrogen, and no such substitution can be observed in this case. The acid prepared is the α-lactic acid, $CH_3CH(OH)COOH$.

We can also prepare α-lactic acid from propionic acid, CH_3CH_2COOH, by acting first with chlorine, which substitutes chlorine for hydrogen in the α-position forming α-chloropropionic acid, $CH_3CHClCOOH$, following this by the substitution of hydroxyl for chlorine by the action of potash.

These two methods of preparation are both general for oxy-acids. The α-lactic acid, sometimes called ethylidene lactic acid, is found to be identical with the natural fermentation lactic acid. It is a thick hygroscopic syrup which gives off water when heated, forming an anhydride. It is split up by dilute acids into a mixture of aldehyde and formic acid, and it is oxidised to acetic and carbonic acids, both of which reactions confirm the suggested formula of α-lactic acid.

The β- or ethylene lactic acid, $CH_2(OH)CH_2COOH$ can be prepared from glycerin by methods which consist generally in substituting chlorine for hydrogen in the β-position, followed by the substitution of hydroxyl for the chlorine. The first step is more difficult than the corresponding step in the formation of the α-acid. The β-acid forms no anhydride on heating. It is oxidised with the formation of carbonic and oxalic acids.

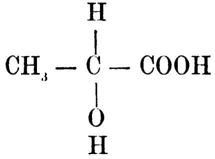
332. Optical Activity.—Sarcolactic acid prepared from muscular tissue is chemically the same as ordinary lactic acid, but it possesses a curious action upon light, which is best observed in the case of light whose vibrations are in one plane or in parallel planes.

Such light, which is said to be *polarised*, is produced by passing a beam of light through certain crystals such as those of Iceland spar or tourmaline, or by reflecting the beam by a glass surface inclined at a definite angle to the direction of the beam. The beam is so affected by the crystal or surface that it is resolved into components vibrating in directions at right angles, and both components are polarised. For convenience only one of the components is used, the other being got rid of.

The plane in which the light vibrates or is polarised can be identified by the fact that the polarised light will pass almost unchanged through a crystal set parallel to the original, while it will not pass through a crystal set at right angles to the original direction.

When polarised light is passed through a solution of sarcolactic acid its plane of vibration or polarisation appears to become twisted, so that the light will not pass through the second crystal unless that is rotated through a measurable angle. Sarcolactic acid is said to *rotate the plane of polarisation of light* or to possess *optical activity.*

The property appears to be connected with a special twist in the arrangement of the atoms within the molecule, and is usually associated with the presence of one or more carbon atoms which have four different atoms or groups attached to them, and which are called *asymmetric carbon atoms* ; in the case of α-sarcolactic acid the formula can be arranged to show this, thus,



$$\begin{array}{c} H \\ | \\ CH_3 - C - COOH \\ | \\ O \\ H \end{array}$$

β-lactic acid does not contain an asymmetric carbon atom, and is not optically active.

Now while sarcolactic acid is optically active and rotates the plane of polarisation of light through a right-handed or positive angle, *i.e.* is *dextro-rotatory*, common lactic acid is optically inactive. The latter is, however, half converted into the sarcolactic variety by the action of the blue mould, *Penicillium glaucum*, while the other half is used up by the mould. When separated, the ordinary inactive acid is found to be a mixture of equal parts of the dextro-rotatory sarcolactic acid and a *laevo-rotatory* acid of equal rotatory power in the left-handed or negative direction.

333. Salicylic Acid.—When wintergreen oil is boiled with caustic soda, in order to obtain methyl alcohol, and the caustic soda solution is acidified with hydrochloric acid, a silky white precipitate is formed. This precipitate dissolves readily in alkalies to form one series of salts only, and is an acid, *salicylic acid.* It has the percentage composition and molecular weight represented by the formula $C_7H_6O_3$, and is a hydroxy derivative of benzoic acid represented by $C_6H_4(OH)COOH$. Salicylic acid is a colourless crystalline solid, almost insoluble in water but soluble in alcohol. It acts as a preservative of fermentable substances, but as it is poisonous it is not allowed to be used in food ; it is used in medicine.

Exp. 381.—(*a*) Heat a little salicylic acid with quicklime in a small test-tube and notice the smell of phenol.

(*b*) Take some salicylic acid and pour some caustic soda solution on it, it readily dissolves ; add some dilute hydrochloric acid, the acid is preciptated.

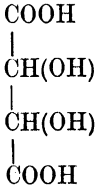
(*c*) To a solution of salicylic acid in a minimum quantity of alkali add some ferric chloride solution. A violet colour is formed.

(*d*) Add some bromine water to some salicylic acid solution; a white precipitate is formed.

334. Tartaric Acid.—When the juice of ripe juicy fruits is evaporated, crystals generally separate mixed with sugar. The crystals dissolve in water, and may be purified by re-crystallisation in presence of dilute sulphuric acid or carbonic acid, which makes the crystals less soluble.

However, in the natural fermentation of grape juice carbon dioxide is formed, which causes the precipitation of the same insoluble crystalline substance, *tartar*, which yields potassium carbonate on ignition. The body is recrystallised and forms *cream of tartar*. When heated it chars and forms potassium carbonate, so it appears probable that the original body is a potassium salt of an organic acid. Cream of tartar is dissolved in water, and precipitated as a lead or calcium salt, which is suspended in water and decomposed by sulphuretted hydrogen in the former case and by sulphuric acid in the latter. The solution is evaporated and deposits crystals of an acid body of a composition represented by $C_4H_6O_6$, called *tartaric acid.*

Tartaric acid forms two series of salts, and two only, with different amounts of caustic potash solution, so that it is probably a dibasic acid, containing two carboxyl groups. It is acted on by hydrobromic acid with the substitution of two bromine atoms for two hydroxyl groups, so that it probably contains two alcoholic hydroxyl groups. The best way in which a formula can be arranged to agree with this is



$$\begin{array}{l} \mathrm{COOH} \\ | \\ \mathrm{CH(OH)} \\ | \\ \mathrm{CH(OH)} \\ | \\ \mathrm{COOH} \end{array}$$

The presence of so many hydroxyl groups causes instability under the action of heat, sulphuric acid, and oxidising agents, even silver salts being reduced by the acid.

Exp. 382.—(*a*) Heat some crystals of tartaric acid alone and with concentrated sulphuric acid, and notice the decomposition products.

(*b*) Shake up a silver solution with ammonia and soda as in Exp. 368, and add some cream of tartar solution. Warm and observe the silver mirror.

The two tartrates of potassium are of interest, the normal salt, $K_2C_4H_4O_6$, $\frac{1}{2}H_2O$, being soluble, and the acid salt, cream of tartar, $KHC_4H_4O_6$, being rather insoluble in water. Rochelle salt, a double tartrate of sodium and potassium, $KNaC_4H_4O_6$, $4H_2O$, is useful on account of its solubility.

The tartrates of the heavy metals are interesting as they are insoluble in water but soluble in cream of tartar solution, with formation of soluble double tartrates. These double tartrates are also soluble in excess of alkali, so that they prevent the precipitation of these metals by alkalies.

Use is made of this property in making up an alkaline solution of a copper salt, *Fehling's solution*, and in making up soluble preparations of iron and of antimony.

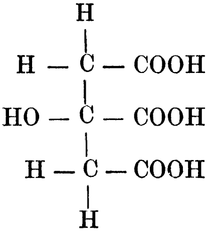
Exp. 383.—(*a*) To a solution of a potassium salt add a solution of tartaric acid, and rub the inside of the containing vessel with a glass rod. The insoluble acid salt, hydrogen potassium tartrate, cream of tartar, separates out.

(*b*) To a solution of ferric chloride add tartaric acid in excess, and then add excess of ammonia solution. The solution turns brown, but no precipitate of ferric hydroxide is formed.

(*c*) To a solution of copper sulphate add Rochelle salt and then caustic potash in excess. No precipitate appears even on boiling, though the solution turns to the blue colour characteristic of alkaline solutions of copper. This solution is Fehling's solution.

335. Citric Acid.—Lemon juice is acid, and when it is neutralised with chalk and boiled with lime colourless crystals gradually separate out. If the crystals are decomposed by boiling with dilute sulphuric acid, and the solution is filtered and concentrated by boiling, clear colourless crystals separate out. These crystals have a percentage composition agreeing with the formula $C_6H_8O_7$. They are strongly acid, and are called *citric acid*.

Citric acid forms three series of salts and is a tribasic acid, so that it contains three carboxyl groups. It also contains an alcoholic hydroxyl group replaceable by bromine and it is represented by the formula



$$\begin{array}{ccc} & H & \\ & | & \\ H - & C & - COOH \\ & | & \\ HO - & C & - COOH \\ & | & \\ H - & C & - COOH \\ & | & \\ & H & \end{array}$$

A characteristic property of citric acid is the formation of soluble double salts in which two bases replace the hydrogen atoms of different carboxyl groups, thus the soluble calcium ammonium citrate is represented by the formula

$$C_3H_4(OH)(COO)_2Ca\ COO(NH_4).$$

Citric acid occurs in oranges and many other fruits besides lemons, and is also found in plants such as the vetch, pea, etc.

CHAPTER XXVIII.

ETHEREAL SALTS : SAPONIFICATION.

336. Ethereal Salts or Esters.—We have seen that wintergreen oil is decomposed by alkalies yielding methyl alcohol, *i.e.* an organic base, and salicylic acid, an organic acid. Many other natural oils and fats are similarly decomposed, yielding other alcohols and other acids. Such salts of organic bases and organic acids are called *ethereal salts* or *esters.*

We might at first expect that the resemblance between organic and inorganic acids and bases would be so complete that mere addition of an alcohol to an acid would cause neutralisation, accompanied by the formation of an organic salt and water.

Exp. 384.—Place about 20 gm. of oxalic acid crystals in a basin in a water oven or over a water bath and heat until they have lost about $\frac{1}{4}$ of their weight. The acid is now anhydrous. Place the anhydrous acid in a distilling flask together with about 20 gm. of alcohol (or pure methylated spirit). Heat carefully for, say, $\frac{1}{2}$ hour just to the boiling point, and then raise the temperature. Collect the distillate boiling above about 125° C. and redistil it, collecting the fraction boiling at about 180°—190° C. Examine and smell the liquid, boil a few drops with water and test for alcohol by the iodoform test (Exp. 362), and for oxalic acid by calcium chloride. Add a solution of ammonia to some of the liquid.

The liquid thus prepared has an ethereal smell and boils at 186° C. It is decomposed by water into oxalic acid and ethyl alcohol, as is indicated by the iodoform test and the formation of a precipitate of calcium oxalate on the addition of calcium chloride after boiling the liquid with water in Exp. 384. It yields with aqueous ammonia a white precipitate which will be examined later. The liquid is a salt of alcohol and oxalic acid called *ethyl oxalate* or *oxalic ester*, and is represented by the formula

$$\begin{array}{l} COO(C_2H_5) \\ | \\ COO(C_2H_5) \end{array}$$

Since the water formed by the reaction between the acid and the alcohol tends to decompose the ester the preceding method is not of general application, and in order to form the salt we require the presence of a dehydrating agent of some kind. The two reagents generally used are concentrated sulphuric acid or hydrochloric acid gas.

Exp. 385.—Fit a distilling flask with a thermometer and condenser, as in Fig. 90. Make a mixture of 50 c.c. of alcohol (methylated spirit), 32 c.c. of glacial acetic acid, and 9 c.c. of strong sulphuric acid, and pour it into the flask. Warm the liquid and collect all liquid coming off below 100° C. Pour the distillate into water and shake well: allow to separate, and pour off, separate, or pipette off the more oily upper layer. Redistil this upper layer from solid calcium chloride and collect the fraction boiling at about 74°—75° C. This fraction is *acetic ester.*

337. Acetic Ester.—Acetic ester is a colourless liquid with a pleasant fragrant smell, somewhat like that of cider. Its percentage composition and molecular weight are represented by the formula $C_4H_8O_2$. By the action of concentrated caustic soda solution it is split up into ethyl alcohol, which distils off, and sodium acetate, which remains in solution. This suggests that the body must be considered as *ethyl acetate*, with the formula $CH_3COOC_2H_5$. It is fairly soluble in water (1 in 12), and on standing the water becomes strongly acid from formation of free acetic acid. This decomposition by water, or hydrolysis, gives one explanation of the non-formation of the salt by the action of the free acid on the alcohol, since the water tends to split up the salt as soon as it formed. The equation is generally written thus,

$$CH_3COOH + C_2H_5OH \rightleftarrows H_2O + CH_3COOC_2H_5.$$

The two arrow heads indicate that the direction of the change depends upon the relative proportions of the products, and on the conditions of the reaction.

338. The Nature of Fats. Palmitic and Stearic Acids.—We have already seen that glycerin, an alcohol, is obtained from fat in the process of soap-making, and this throws light upon the nature of fats.

Exp. 386.—Boil some suet with a dilute solution of caustic soda until it is mostly dissolved. Pour off the clear liquid, and add to it an excess of hydrochloric acid. There is an immediate white precipitate of flocks of a fatty substance. Collect some of the precipitate on a filter paper. Mix some of the precipitate with water; it is insoluble. Add soda solution; the precipitate dissolves, and is again precipitated by the action of an acid. The flocks are probably an acid or acids.

Examination of the flocks prepared in this way from different animal fats shows that they are mixtures, and it is possible to squeeze out by pressure a yellow oil, and leave a white wax-like solid.

The yellow oil consists for the most part of an oil represented by the formula $C_{17}H_{33}COOH$, and called *oleic acid.*

The white solid differs in composition with its source. Thus the solid obtained from hard fat and Shea butter has a composition represented by $C_{17}H_{35}COOH$, and is called *stearic acid*, while that obtained from softer fats and Japanese wax has a composition represented by $C_{15}H_{31}COOH$, and is called *palmitic acid.*

The last two acids are paraffins with a carboxyl group substituted for hydrogen, and the first is an olefine with one pair of trivalent carbon atoms or a double bond.

The properties of palmitic and stearic acids are so similar that they are generally considered together. They are colourless fatty bodies, melting at 61° and 71° C. respectively. They are insoluble in water, soluble in alcohol, benzene, etc., and in solutions of alkalies. They combine with bases to form salts, the *soaps.*

339. Soaps.—The soluble alkali soaps are soluble in pure water, but insoluble in salt water.

Exp. 387.—Make a solution of curd soap in water and add to it some salt. The soap comes out of solution in the form of flocks, which rise to the surface. Filter off some of the flocks and boil them with water; they are soluble in pure water, so that they are not fatty acids.

The soaps of calcium and magnesium are insoluble in water, and are precipitated by the addition of soap solution to hard water. This precipitation is quantitative, and is used for the estimation of hardness of water.

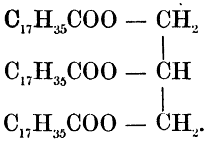
The sodium soaps are harder than the potassium soaps, so that the latter are generally called *soft* soaps.

Soap solution has a curious effect on the surface tension of fats and oils, so that finely divided particles of fats do not tend to run together quickly in a soapy solution. Such an intimate mixture of fat particles and water is termed an *emulsion*, and the cleansing properties of soap are due to the formation of an emulsion of any particles of grease by the action of the soapy water.

This peculiar action upon the surface tension of liquids is now considered to be connected with the shape of the molecules of the fatty acids, which in the surface of water appear to arrange themselves in such a way that the CH_3 group ends of the carbon chains take up a position nearer to the surface than the COOH group ends, which are attracted towards the water. At the surface, therefore, the carbon chains will be on the whole at right angles to the surface, with the COOH groups pointing towards the water. The full effect of soap in lowering the surface tension of water takes some hours to show itself, which can be accounted for by the time taken by the molecules in taking up their position.

The soap itself tends to separate out from a concentrated solution below a certain temperature in a network of strings, again suggesting that in the molecule the carbon chain does not tie itself into knots but tends to keep more or less in a straight line.

Since glycerin and fatty acids are prepared by splitting fats by the action of caustic soda, we believe that the common fats are compounds of glycerin with the acids, palmitic, stearic, and oleic, and since glycerin is a triacid base, we should expect the formula of the stearic acid fat to be



$$\begin{array}{l} C_{17}H_{35}COO - CH_2 \\ \qquad\qquad\qquad\;\; | \\ C_{17}H_{35}COO - CH \\ \qquad\qquad\qquad\;\; | \\ C_{17}H_{35}COO - CH_2. \end{array}$$

This agrees with the percentage composition of this fat, which is called *stearin* or *tristearin*. Similar formulae are given to *tripalmitin* and *triolëin*, *i.e.* $(C_{15}H_{31}COO)_3C_3H_5$ and $(C_{17}H_{33}COO)_3C_3H_5$, respectively.

The process of splitting a neutral fat by the action of a base, forming a soap and glycerin, is termed *saponification*, but the term is extended to include the splitting of a neutral body into base and acid generally.

340. Esters of Palmitic and Stearic Acids.—Palmitic and stearic acids, being paraffins with a carboxyl group substituted for hydrogen, are members of the acetic series, and it is instructive to compare the properties of the higher and lower acids, their changes of melting point, boiling point, solubility in water, etc.

Just as it is possible to make an ethyl ester from acetic acid, so it is possible to do the same with palmitic and stearic acids, by passing hydrochloric acid gas into alcoholic solutions of the acids. These esters, represented by the formulae

$$C_{15}H_{31}COOC_2H_5 \quad \text{and} \quad C_{17}H_{33}COOC_2H_5,$$

are crystalline bodies melting at 24° and 33° C., respectively.

CHAPTER XXIX.

NITROGEN COMPOUNDS.

341. Amines.—An examination of products of putrefaction, herring pickle, fungi, and many other bodies, by heating them with solutions of caustic alkali, causes them to give off substances with a characteristic blended smell of ammonia and fish. These bodies readily dissolve in water, to which they impart their smell and the property of turning litmus blue. Their solutions resemble ammonia solution in being neutralised by acids with the formation of colourless, crystalline salts.

Similar bodies are formed when the chlorine, bromine, or iodine derivatives of the hydrocarbons are heated with an alcoholic solution of ammonia.

Thus, when methyl iodide, CH_3I, is heated with an alcoholic solution of ammonia under pressure a solid residue is obtained after evaporation; this is a mixture of five substances which can be separated only by a somewhat complicated method. The substances are found to have the formulae $NH_3(CH_3)I$, $NH_2(CH_3)_2I$, $NH(CH_3)_3I$ and $N(CH_3)_4I$ respectively, and are mixed with ammonium iodide, NH_4I.

From the appearance of these formulae we should expect that the substances would resemble ammonium salts and be decomposed by caustic soda solution. It is found that caustic soda does decompose the first three, forming sodium iodide and liberating gases which resemble ammonia in properties and may be considered as ammonia in which hydrogen atoms are replaced by the radicle methyl. Such bodies are called *amines*, and these are *methylamines*, their salts being called *methylammonium salts*.

Thus the first of the above bodies, $NH_3(CH_3)I$, is called methylammonium iodide, and yields, under the action of soda, methylamine, NH_2CH_3. The second, $NH_2(CH_3)_2I$, is called dimethylammonium iodide and yields $NH(CH_3)_2$, dimethylamine. The third, $NH(CH_3)_3I$ is trimethylammonium iodide and yields trimethylamine, $N(CH_3)_3$. The fourth, which is not decomposed by soda, is $N(CH_3)_4I$, tetramethylammonium iodide.

Other important methods are available for preparing amines, for example :—

(*a*) The action of nascent hydrogen on a nitro compound of a hydrocarbon, when two hydrogen atoms are substituted for two oxygen atoms—a rather unusual exchange, though not quite unexpected, since two atoms of hydrogen can combine with two atoms of oxygen to form hydrogen peroxide, H_2O_2. To take the case of ethylamine, ethyl iodide is digested with silver nitrite and nitro ethane is formed. Using an equation,

$$C_2H_5I + AgNO_2 = C_2H_5NO_2 + AgI.$$

By the action of nascent hydrogen (iron and acetic acid may be used) this is reduced to ethylamine, $C_2H_5NH_2$.

(*b*) The action of nascent hydrogen on a cyanide or nitrile (see Art. 345). In this case, the carbon atom of the cyanide forms part of the hydrocarbon radicle after reduction, so the ethylamine is made by the reduction of methyl cyanide, thus,

$$CH_3CN + 2\,H_2 = CH_3CH_2NH_2.$$

It will be noted that the second method gives us only one amine at a time, so they can be readily identified. These reactions seem to point to a close connection between the classes of nitrogen derivatives of organic bodies.

The methylamines are liquids with a fishy smell of ammonia. They combine with acids to form salts, and their chlorides are like ammonium chloride in combining with platinic chloride to form platino-chlorides, *e.g.* $(NH_3CH_3)_2PtCl_6$, from methylamine, NH_2CH_3. These salts are used to determine the molecular weights of the amines.

The salts are saponified by caustic soda, except tetramethylammonium iodide, $N(CH_3)_4I$, which, however, yields a free base, tetramethylammonium hydroxide, $N(CH_3)_4OH$, by the action of moist silver hydroxide.

Just as ammonia is oxidised by nitrous acid to water and free nitrogen, so the amines are oxidised by nitrous acid to alcohols and free nitrogen. Thus methylamine yields methyl alcohol when heated with nitrous acid.

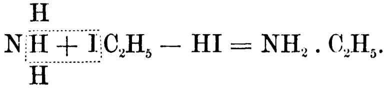
$$NH_2(CH_3) + HNO_2 = CH_3OH + N_2 + H_2O.$$

Compare

$$\begin{aligned} NH_3 \quad + HNO_2 &= HOH + N_2 + H_2O \\ &= N_2 + 2\,H_2O. \end{aligned}$$

A very characteristic reaction of many amines is the production of an iso-nitrile smell on heating with chloroform and caustic soda, see Exp. 355.

Starting with the mode of formation of the ethylamines from ammonia by the action of ethyl salts, we have considered the amines as derived from ammonia by the substitution of an organic radicle for hydrogen, thus,

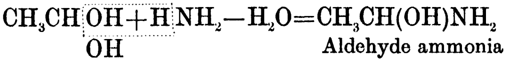


$$N\overset{H}{\underset{H}{\boxed{H + I}}}C_2H_5 - HI = NH_2\,.\,C_2H_5.$$

But it is also possible to look at the amines as derivatives of the alcohols in which the group ($-NH_2$), the *amido group*, replaces hydroxyl, with the formation of water, thus,

$$C_2H_5\boxed{OH + H}NH_2 - H_2O = C_2H_5NH_2.$$

Looked at from this point of view we should expect the other hydroxyl derivatives of the hydrocarbons, viz. the aldehydes and acids, to combine with ammonia and split off water. We find that this is the case, the aldehydes forming the compounds *aldehyde ammonias*, and the acids ammonium salts and compounds called *amides*, thus,



$$CH_3CH\underset{OH}{\boxed{OH+H}}NH_2-H_2O=CH_3CH(OH)NH_2$$

Aldehyde ammonia

$$CH_3CO\boxed{OH+H}NH_2-H_2O=CH_3CONH_2.$$

Acid amide

Aldehyde ammonia need not be further considered, so that there only remains the last class, the *acid amides*.

342. Amides. Acetamide.—To take the simple case of acetic acid, ammonia readily reacts with acetyl chloride, CH_3COCl, to form *acetamide*, CH_3CONH_2, in which the amido group may be looked upon as taking the place of a chlorine atom in the chloride, or the acid group *acetyl* (CH_3CO —) as taking the place of a hydrogen atom in ammonia.

Exp. 388.—Distil some ammonium acetate in a small retort (Fig. 99). After a time a solid with a smell of mice condenses in the neck of the retort. This is acetamide.

By heating ammonium acetate it splits off water, and finally forms acetamide, thus,

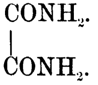
$$CH_3COONH_4 = CH_3CONH_2 + H_2O.$$

The acid amides are converted back again into ammonium salts by boiling with water.

343. Oxamide.—In the case of oxalic acid the amide may be prepared in another way, by the addition of an aqueous solution of ammonia to oxalic ester.

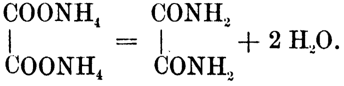
Exp. 389.—Shake some oxalic ester with a solution of ammonia. Filter off the white precipitate and test by boiling with caustic soda. Test the vapour with litmus paper and the solution for oxalic acid.

We note that by the action of ammonia on oxalic acid a white insoluble solid is formed, and that this solid is converted into oxalic acid and ammonia by the action of alkalies. The solid is *oxamide* and it is represented by the formula $(CONH_2)_2$ or



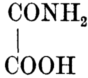
$$\begin{array}{l}CONH_2.\\ |\\ CONH_2.\end{array}$$

Oxamide is also formed when ammonium oxalate is heated, thus,—



$$\begin{array}{l}COONH_4\\ |\\ COONH_4\end{array} = \begin{array}{l}CONH_2\\ |\\ CONH_2\end{array} + 2\,H_2O.$$

Oxalic acid, however, is dibasic, and if we heat the acid ammonium oxalate, another amide is formed containing a carboxyl group; this is *oxamic acid*,



$$\begin{array}{c} CONH_2 \\ | \\ COOH \end{array}$$

, and is typical of a large number of substances obtained from plant and animal structures, the *amido acids.*

One of the best known of such substances is *asparagin*, contained in asparagus, peas, beans, vetches, and other young shoots. Asparagin is derived from *succinic acid*, a dibasic acid containing four carbon atoms with the formula $COOH - CH_2 - CH_2 - COOH$, and it is an acid amide and an amine at the same time. It is an amido succinamic acid represented by $COOH - CH(NH_2) - CH_2 - CONH_2$. As it is an amine and an acid, it possesses both basic and acid properties.

344. Urea.—One most important amide from the physiological point of view is *urea.*

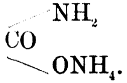
When urine is evaporated down, long rhombic prisms separate out, which are called urea, and are soluble in alcohol, but not in ether. The crystals melt at 132° C. and sublime in vacuo. When analysed they are found to be represented by the formula CON_2H_4, or possibly some multiple of that.

When urea is heated it gives off ammonia. (It forms several compounds in succession, biuret, cyanuric acid, and cyanic acid.)

Alkalies decompose urea, forming a carbonate of the alkali and setting free ammonia. Hence, since urea splits up into carbon dioxide and ammonia, it is possibly connected directly with them.

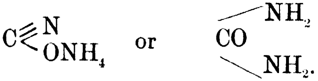
Exp. 390.—Fill a jar with ammonia gas and another with carbon dioxide, and place them mouth to mouth.

The ammonia and carbon dioxide combine to form a white solid which is not ammonium carbonate, though it is readily converted into that salt by the action of water. It may be represented by the formula CO_2, $2\,NH_3$. It has been proved that the two nitrogen atoms are not situated similarly in the molecule, so that the formula must be written as that of a ammonium salt, *ammonium carbamate*,



$$CO\begin{matrix}NH_2\\ONH_4\end{matrix}.$$

Phosphorus pentoxide dehydrates this salt, forming urea which may thus be,



$$C\begin{matrix}\equiv N\\-ONH_4\end{matrix}\quad\text{or}\quad CO\begin{matrix}NH_2\\NH_2\end{matrix}.$$

The first formula represents it as ammonium cyanate (p. 342) the second as the amide of carbonic acid, *carbamide*.

(Urea may also be prepared by the action of phosphorus pentoxide, or a temperature of 135° C., on ammonium carbonate.)

Urea combines directly with acids to form salts, of which the most characteristic are the nitrate and the oxalate; these should be examined under a microscope. It is decomposed by nitrous acid with the formation of carbon dioxide, nitrogen, and water. Hypochlorites and hypobromites also oxidise urea with formation of the same products; in these reactions the volume of nitrogen given off bears a nearly constant relation to the amount of urea taken, so that the last is used for the quantitative estimation of urea.

Mercuric nitrate forms a white precipitate with urea, which is approximately constant in composition, and is represented by $2\,CO(NH_2)_2,\ Hg(NO_3)_2,\ 3\,HgO$. The precipitate removes all the urea from a solution, and is used in the estimation of urea by Liebig's volumetric method.

345. Cyanogen Compounds.—We have now to deal with a very important class of organic bodies, the *cyanogen compounds*, which contain nitrogen combined with carbon. We have already noticed one important use of these bodies in the synthesis of organic acids.

When electric sparks are passed through a mixture of acetylene and nitrogen they partly combine to form a gas which smells of bitter almonds, and is soluble in caustic soda solution. The gas is obtained in a purer form from the solution in caustic soda by the action of dilute sulphuric acid.

The gas is more conveniently obtained from bitter almonds themselves.

Exp. 391.—Pound 2 or 3 bitter almonds in a mortar, add water and mix them well up; allow the mixture to stand in a warm place. After a few hours place the mixture in a flask fitted with a condenser and distil. Be careful to do the distillation in a draught chamber, and not to inhale the fumes.

The distillate contains a volatile acid, having the percentage composition and molecular weight represented by the formula HCN, and called *hydrocyanic* or *prussic acid.* The formation of the acid is accompanied by the formation of glucose and oil of bitter almonds or benzaldehyde, and these are all derived from a compound of the three bodies, a *glucoside*, *amygdalin*, $C_{20}H_{27}NO_{11}$, which may be dissolved out of the almonds by cold water. The equation which represents the reaction is:

$$\underset{\text{Amygdalin}}{C_{20}H_{27}NO_{11}} + 2\,H_2O = \underset{\text{Benzaldehyde}}{C_6H_5 - CHO} + 2\,\underset{\text{Glucose}}{C_6H_{12}O_6} + HCN.$$

To obtain the pure acid, the dilute solution is mixed with calcium chloride and distilled, when it is found to form a colourless liquid solidifying at — 15° C. and boiling at 26·5° C. It has a characteristic smell of bitter almonds or laurel leaves, and is one of the most poisonous bodies known, as regards animal life, either in a state of vapour or in solution. It burns in air when lit. Hydrocyanic acid is soluble in water, and combines with bases to form salts in which the one hydrogen atom is replaced by the metal of a base.

On mixing caustic potash with excess of hydrocyanic acid and evaporating the solution we obtain a colourless deliquescent solid, *potassium cyanide*, KCN. The salt is very soluble in water and also, but to a less extent, in alcohol. It is a very poisonous salt. As hydrocyanic acid is a weak acid, potassium cyanide smells of prussic acid, since the carbon dioxide of the air forms a strong enough acid in presence of water vapour to decompose the salt.

Potassium cyanide precipitates other metallic cyanides from solution, *e.g.* silver and mercuric cyanides, AgCN and $Hg(CN)_2$, but these cyanides readily dissolve in excess of the potassium salt though they are insoluble in water. The explanation of this change of solubility is that double salts of silver or mercury and potassium are formed, which are soluble in water.

Exp. 392.—To a solution of silver nitrate add potassium cyanide solution.

A white precipitate is formed of silver cyanide, AgCN ; as excess of the cyanide solution is added the precipitate dissolves, forming the double salt, AgCN, KCN.

Just as mercuric oxide is split up by heat into a mixture of mercury vapour and oxygen, so mercuric cyanide is split up into a mixture of mercury vapour and another gas, which smells very like prussic acid, and burns with a lavender flame. This gas has the molecular composition represented by the formula C_2N_2, and is called *cyanogen.*

The equation which represents the greater part of the reaction is

$$Hg(CN)_2 = Hg + (CN)_2$$

which may be compared with the corresponding equation for the decomposition of mercuric oxide,

$$2\,HgO = 2\,Hg + O_2.$$

The gas is very poisonous and should only be prepared with the greatest precautions.

The existence of cyanogen enables us to show the resemblance in properties between the *element chlorine* and the *compound radicle cyanogen.*

(*a*) Cyanogen combines with metals directly to form cyanides ; in the case of sodium we may compare the action with that of chlorine :

$$2\,Na + (CN)_2 = 2\,NaCN$$
$$2\,Na + Cl_2 = 2\,NaCl.$$

(*b*) Cyanogen forms a hydride which has acid properties and forms salts from which the hydride is prepared by the action of less volatile acids. This is also the case with chlorine.

$$NaOH + HCN = NaCN + H_2O$$
$$NaOH + HCl = NaCl + H_2O.$$

(*c*) The action of cyanogen on a caustic alkali is similar to that of chlorine, involving both an oxidation to the state of *cyanic acid* and a reduction to the state of hydrocyanic, thus :—

$$2\,NaOH + (CN)_2 = NaCN + NaCNO + H_2O,$$
$$2\,NaOH + Cl_2 = NaCl + NaClO + H_2O.$$

One of the most important properties of the cyanides, as we have just seen, is their tendency to form double salts, but in the case of the cyanides of iron and other related metals these salts are even more characteristic, and are considered as salts of new compound acids.

Exp. 393.—To a solution of ferrous sulphate add potassium cyanide solution. A brown precipitate of ferrous cyanide is seen. Add excess of the potassium salt, and the precipitate gradually dissolves forming a yellow solution. Filter the solution and evaporate down; yellow crystals separate out. These crystals are potassium ferrocyanide.

Potassium ferrocyanide, $4\,KCN,\ Fe(CN)_2, 3\,H_2O$ or $K_4FeC_6N_6\ 3\,H_2O$, is a most important salt, and it is the chief commercial source of the cyanogen compounds.

Chlorine oxidises potassium ferrocyanide in solution by removing one atom of potassium. The salt formed is called potassium ferricyanide, and is usually given the double formula, $K_6Fe_2C_{12}N_{12}$, though there does not seem to be any adequate reason for preferring this formula to the simpler $K_3FeC_6N_6$. The equation representing its formation may be given :—

$$2\,K_4FeC_6N_6\ Aq + Cl_2 = 2\,K_3FeC_6N_6\ Aq + 2\,KCl\ Aq.$$

Exp. 394.—To solutions of potassium cyanide and potassium ferrocyanide add silver nitrate and ferric chloride solutions, and compare the results.

Exp. 395.—To solutions of ferrous sulphate and potassium ferrocyanide add ammonium chloride and ammonia.

The ferrocyanide does not give the cyanide reactions nor the ferrous tests, and so is not an ordinary double salt.

Exp. 396.—Heat some potassium ferrocyanide with concentrated sulphuric acid and collect the gas given off over water.

The gas burns with a blue flame, forming carbon dioxide; it is carbon monoxide.

Exp. 397.—To solutions of potassium ferrocyanide and ferricyanide add ferrous and ferric salts.

Note that no precipitate is formed of ferric ferricyanide, and that all the other mixtures give blue precipitates; ferric ferrocyanide is Prussian blue.

The organic cyanides, also called *nitriles*, have already been mentioned as of great importance in the synthesis of organic acids. They are prepared by two separate methods.

(i) By the action of potassium cyanide on the haloid derivatives of the hydrocarbons in alcoholic solution, or by the distillation of the acid sulphates of the alcohols or the sulphonates of the benzene compounds with potassium cyanide or ferrocyanide. Equations may be given :—

$$CH_3I + KCN = CH_3CN + KI$$

$$C_6H_5 . KSO_3 + KCN = C_6H_5CN + K_2SO_3.$$

It has already been noticed that this reaction is characterised by the addition of one carbon atom to the molecule.

(ii) By the removal of water from the ammonium salts of the organic acids by phosphorus pentoxide. Thus, in the case of ammonium acetate, methyl cyanide is formed,

$$CH_3COONH_4 - 2\ H_2O = CH_3CN.$$

No change in the number of carbon atoms is noted here.

As we have already seen, water, dilute acids, and alkalies saponify the cyanides into ammonia and an organic acid. In the case of methyl cyanide, ammonium acetate is reformed,

$$CH_3CN + 2\ H_2O = CH_3COONH_4.$$

Nascent hydrogen converts the cyanides into *amines*. Thus methyl cyanide is converted into ethylamine.

346. Cyanic Acid and Cyanates.—We have already noted that cyanogen resembles chlorine in forming a mixture of a cynanate and a cyanide by its action upon caustic alkalies. But cyanates are more easily prepared by the direct oxidation of cyanides by melting them with an oxidising agent such as the peroxide of lead or manganese.

An equation which represents the change is

$$2\,NaCN + PbO_2 = 2\,NaCNO + Pb.$$

It will be noted that the oxide is reduced to metal.

Cyanic acid is very unstable; in a free state it rapidly forms triple molecules of *cyanuric acid*, $H_3C_3N_3O_3$, which is soluble in ether, so that the decomposition of sodium cyanate by hydrochloric acid in presence of ether yields cyanuric acid from the ethereal solution. When this is heated and passed into ether with dry ammonia, ammonium cyanate is formed, and may be obtained by evaporating the ether in the cold; but if water is added before evaporation or if the ethereal solution is heated then crystals of urea only are formed.

Ammonium cyanate, NH_4CNO, and urea, CON_2H_4, have the same molecular composition, so that there is evidently an isomeric transformation from ammonium cyanate to urea. This change was first observed by Wöhler in 1828, and marks the first synthesis of an organic compound from inorganic substances.

The isomeric change of the cyanic acid group NCOH into the group HNCO appears to be of great importance in the chemical changes of living matter.

347. The Chemistry of Living Matter.—A complete explanation of the chemistry of living matter is at present beyond the knowledge of the chemist, but the problem has been and is being attacked on various lines which may eventually lead to the desired goal. Thus a great deal is known of the chemical products which take part in the building up of protoplasm and of the ways in which they combine, and also of the products obtained by splitting up protoplasm in the body and in the laboratory. The compounds which most nearly approach to protoplasm possess similar properties, whether derived from animal or vegetable structures, and are called *proteins.*

Proteins are complicated chemical structures containing hundreds of atoms in their molecules, and they are stored by plants for use by the growing seedlings, as well as forming the basis of animal tissues. Proteins from different sources vary considerably in properties, but they agree in containing nitrogen, carbon, hydrogen, and oxygen in their molecules, in being coagulated by heat, and in being split up by the action of *enzymes* (see Art. 355) in digestive processes.

Exp. 398.—Boil a small quantity of white of egg (egg albumen) with water.

Boil a small quantity of white of egg with nitric acid, cool, and neutralise with caustic soda.

Add excess of caustic soda to a small quantity of white of egg, and then one drop of copper sulphate solution.

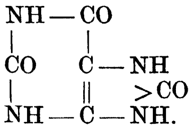
We note that egg-albumen is coagulated by heat, is turned yellow by nitric acid, and then orange by caustic soda (the xanthoproteic test), and turns copper sulphate in excess of caustic soda a violet colour. These are common *tests for proteins.*

Proteins are split up by the enzymes contained in the digestive juices and yield a great number of recognisable compounds, many of which belong to the class of amido acids and acid amides. By the action of the animal body they are mostly converted into carbonic acid, urea, and derivatives of urea, one of the most characteristic of which is *uric acid.*

Exp. 399.—Place a crystal of uric acid in a porcelain basin and add a drop of nitric acid, evaporate to dryness, and add a drop of caustic soda solution.

On drying, the uric acid gives an orange colour which is turned purple by the alkali (the murexide test).

Uric acid has the formula $C_5H_4N_4O_3$, and is derived from an acid $COOH - CO - COOH$, *mesoxalic acid,* by combination with urea; it is represented by the structural formula



The compounds formed by building up molecules are more difficult to follow, and must be left for more advanced study, but the student may be encouraged to follow the developments of this subject even with a small knowledge of the components which are gradually being built into a foundation for the final structure of living matter, and to appreciate the development of the study of nutrition from a chemical point of view.

CHAPTER XXX.

THE CARBOHYDRATES.

348. The Sugars.—Among the solid products obtained from plants we find a large number which have characteristic aldehyde reactions. These are sweet bodies which crystallise out of plant or fruit juices and are called *sugars*. Other sugars are also obtained from animals, notably the sugar contained in milk and prepared by the evaporation of whey.

Though it has not been possible to convert the sugars into vapour without decomposing them, their molecular weights have been determined by other methods.

Examining the percentage compositions of typical sugars, *e.g.*:—

	Grape Sugar.	Cane Sugar.
Carbon	40·00	42·11
Hydrogen	6·67	6·43
Oxygen	53·33 = 8 × 6·67	51·46 = 8 × 6·43
	100·00	100·00

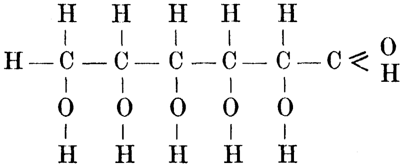
we find that, though the sugars have not all the same composition, yet they agree in having the ratio of oxygen to hydrogen as eight to one, that is, exactly the same ratio as these elements have in water. The composition of grape sugar is apparently the simpler, being represented by CH_2O, or some multiple of it, cane sugar being represented by $C_{12}H_{22}O_{11}$. The multiple in the case of grape sugar, as determined by solution methods of determining molecular weights, is 6, so that grape sugar is $(CH_2O)_6$ or $C_6H_{12}O_6$. Nearly all the sugars of higher molecular weight, when boiled with dilute acids, are changed to bodies of the same percentage composition as grape sugar and with similar properties.

349. Grape sugar, dextrose, or glucose is found in most ripe sweet fruits and in honey, and may be crystallised from fruit juice. It is found as small white hard groups of crystals in raisins. It is a crystalline solid generally containing one molecule of water of crystallisation and melting at 86° C.; when anhydrous it melts at 146° C. Hydrochloric acid acts on it, substituting chlorine for hydroxyl and forming chlorides. Nitric acid has a similar action, forming nitrates, so that grape sugar is basic, and probably alcoholic, in character. It dissolves in sulphuric acid, but is not readily charred by it. Grape sugar is oxidised by chromic acid, a property of an alcohol though it is also characteristic of an aldehyde.

Exp. 400.—Boil a small quantity of grape sugar solution with ammoniacal silver solution, Fehling's solution, and caustic soda solution respectively.

We note that grape sugar reduces silver salts to the metal, cupric salts to cuprous, and that it is resinified by caustic soda, so that it has the characteristic properties of an aldehyde. It is also reduced to an alcohol by sodium amalgam, and the six carbon atoms generally remain together.

Hence, on the whole, the best formula to sum up the properties of grape sugar should represent its carbon atoms as all connected, and as arranged to form an aldehyde and some alcohol groups. There is one way of doing this readily, viz. :—



$$\begin{array}{ccccccccccccc} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \\ & & | & & | & & | & & | & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C}{<}\begin{matrix}\mathrm{O}\\ \mathrm{H}\end{matrix} \\ & & | & & | & & | & & | & & | & & \\ & & \mathrm{O} & & \mathrm{O} & & \mathrm{O} & & \mathrm{O} & & \mathrm{O} & & \\ & & | & & | & & | & & | & & | & & \\ & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \end{array}$$

or in the abbreviated form $CH_2OH(CHOH)_4CHO$.

A characteristic property of dextrose and similar sugars containing the aldehyde group is the formation of a yellow crystalline compound with a substance called phenyl hydrazine in presence of dilute acetic acid. Such compounds are called *osazones*, and that derived from dextrose is *glucosazone.*

The osazones have definite melting points for each sugar, so that they are used for identification.

Five out of the six carbon atoms in dextrose belong to the asymmetric class, so that we should expect dextrose to act upon polarised light. It does so, and rotates the plane of polarisation to the right, in the direction in which the hands of a watch move, so that it is *dextro-rotatory*.

Dextrose, as we have already seen, is readily fermented by yeast, yielding carbon dioxide, alcohol, and small quantities of glycerin and other products.

350. **Fruit sugar or laevulose** is also found in the juice of ripe sweet fruits and in honey, and remains in solution as a syrup after dextrose has crystallised out. It may also be separated by the addition of lime, with which it forms a less soluble compound than dextrose does ; the lime compound is filtered off, squeezed dry, washed, and then decomposed by carbon dioxide in water. The solution on evaporation yields a syrup which deposits crystals of the sugar after some time. The crystals melt at 95° C.

There are other methods of preparing both dextrose and laevulose, which will be noted later.

Laevulose is represented by the formula $C_6H_{12}O_6$, but shows some differences from dextrose. It is not so readily oxidised as dextrose and, while the latter yields an acid containing 6 carbon atoms, laevulose yields for the most part a mixture of acids containing 4 and 2 carbon atoms respectively, so that it must be considered as a ketone rather than an aldehyde. The structural formula generally assigned to laevulose is

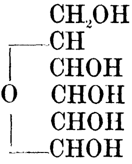
$$CH_2OH\ CHOH\ CHOH\ CHOH\ CO\ CH_2OH.$$

Laevulose contains four asymmetric carbon atoms and it rotates the plane of polarisation of light, but while dextrose rotates the plane to the right, laevulose rotates it to the left, and if equal weights of the two sugars are taken, the laevulose is found to rotate the plane to the left about twice as much as the dextrose rotates it to the right.

351. **Structural Formulae of the Sugars.**—Many other sugars represented by the formula $C_6H_{12}O_6$ are now known.

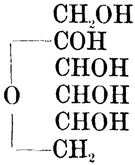
These are found in various plants, and are also prepared by the action of dilute acids, alkalies, and enzymes (see Art. 355) upon sugars of higher molecular weight. They are all grouped together under the name *hexoses*, from the characteristic group of six carbon atoms.

At first sight it might be difficult to account for the differences of properties which distinguish these hexoses, but an examination of the two general structural formulae of dextrose and laevulose shows that it is possible to form many different formulae if we assume that the aldehyde and ketone groups each fundamentally contain two OH groups, as we have seen reason to suppose. The readiness with which these groups split off water suggests one type of isomerism in which the water is split off from two carbon atoms instead of one. Taking this into consideration the following formulae have been selected to represent dextrose and laevulose respectively.



$$\begin{array}{ll} & \mathrm{CH_2OH} \\ \ulcorner & \mathrm{CH} \\ | & \mathrm{CHOH} \\ \mathrm{O} & \mathrm{CHOH} \\ | & \mathrm{CHOH} \\ \llcorner & \mathrm{CHOH} \end{array}$$

Dextrose



$$\begin{array}{ll} & \mathrm{CH_2OH} \\ \ulcorner & \mathrm{COH} \\ | & \mathrm{CHOH} \\ \mathrm{O} & \mathrm{CHOH} \\ | & \mathrm{CHOH} \\ \llcorner & \mathrm{CH_2} \end{array}$$

Laevulose.

Formulae such as these are of the greatest possible importance in studying the building up of plant and animal structures, but the simple formulae first given are sufficient for common use.

352. Scents and Flavours.—A very large number of scents and flavours characteristic of plant and animal products are known. The structure of many of these has been found out, but their investigation is rather a subject for the organic chemist than for the student of agricultural science. Many, *e.g.* turpentine, orange and lemon oils, camphor, peppermint, etc., are found to be derived from complicated hydrocarbons related to benzene, and present interesting problems.

Others are esters, as pear oil, pineapple oil, oil of wintergreen, etc. Others again, such as coumarin, the scent of sweet vernal grass, and vanilla, are found to be derived from aldehydes or ketones; while a large number are found to be compounds of aldehydes and ketones with grape sugar: the last class is that of the *glucosides.*

353. **Bioses or Sucroses.**—Many sugars represented by the formula $C_{12}H_{22}O_{11}$ are known, of which three are of agricultural interest: cane sugar, *sucrose,* malt sugar, *maltose,* and milk sugar, *lactose.* Cane and milk sugars crystallise more readily than most others, and so have been known and used in a pure state for a long time.

354. **Cane Sugar** is obtained from the juice of the sugar cane, sugar beet, or mangold wurzel. The juice is either expressed and evaporated in vacuum pans, or diffused out into water and then evaporated. It is purified by being passed in solution through animal charcoal and then crystallised out.

Cane sugar has a characteristic sweet taste, melts at about 160° C., and dissolves in one-third of its weight of water.

Exp. 401.—(*a*) Boil some cane sugar solution with soda solution and Fehling's solution. Then boil some more cane sugar with dilute sulphuric acid for some time, say half-an-hour, and try these tests again.

(*b*) Pour some strong sulphuric acid on cane sugar.

Cane sugar does not reduce Fehling's solution unless it has been boiled for some time. It is blackened by strong sulphuric acid. It is changed by boiling with dilute sulphuric acid for a short time, and then gives the grape sugar tests at once. It does not form an osazone with phenyl hydrazine.

Analysis shows that cane sugar is split up by dilute acids into a mixture of equal parts of dextrose and laevulose. This reaction may be represented by an equation,

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Dextrose}}{C_6H_{12}O_6} + \underset{\text{Laevulose}}{C_6H_{12}O_6}$$

This kind of chemical change or splitting, produced simply by the addition of water, is called *hydrolysis.*

Cane sugar rotates the plane of polarisation of light to the right, and accompanying the hydrolysis there is a change in the rotation to the left corresponding with the equal proportions of glucose and laevulose. The hydrolysis enables us to fix a formula for cane sugar.

355. **Malt sugar or maltose** is obtained from malt by mixing ground malt with warm water for about 24 hours, and then boiling and crystallising out. It is purified by dissolving in 90 per cent. alcohol. It is not originally present in the barley grain but appears as starch disappears : boiling the malt and water stops the change, and a small quantity of the malt extract is able to convert a very large quantity of starch into maltose. Actions of this kind are said to be due to a ferment or *enzyme*, and the enzyme which produces the above change is called *diastase.*

Maltose is split up or *hydrolysed* by boiling with dilute acids, and each molecule appears to split up into two molecules of grape sugar as represented in the equation

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O = 2\,\underset{\text{Dextrose}}{C_6H_{12}O_6}.$$

Exp. 402.—Repeat Exp. 401, using malt sugar.

Maltose is not so sweet as cane sugar; it melts when rapidly heated at 100° C., but decomposes above that temperature; it reduces Fehling's solution. It rotates the plane of polarisation of light strongly to the right : it splits on hydrolysis entirely into dextrose, and the rotation to the right decreases.

356. **Milk sugar** is easily prepared by the evaporation of whey, the crystals forming readily on strings suspended in the liquid. The crystals contain one molecule of water of crystallisation, and melt at 130° C.

Exp. 403.—Repeat Exp. 401, using milk sugar.

Milk sugar is an energetic reducing agent and reduces ammoniacal silver nitrate solution when only slightly warmed.

It is hydrolysed by boiling with dilute acids into a mixture of equal quantities of dextrose and another sugar of the same class, *galactose*, which is also represented by the formula

$C_6H_{12}O_6$. The equation representing this change is

$$\underset{\text{Milk sugar}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Galactose}}{C_6H_{12}O_6}.$$

The galactose resembles dextrose in being a reducing agent, and it melts at 68° C.

357. Starch and Cellulose.—We have already noted that the starch in malt gradually disappears as maltose appears. Starch is insoluble in cold water, and is found to have the same percentage composition as the insoluble plant product, cotton wool or *cellulose*, viz. :—

Carbon = 44·44
Hydrogen = 6·17
Oxygen = 49·38 = 8 × 6·17.

This percentage composition agrees with the simple formula $C_6H_{10}O_5$, but the molecular weight of the compounds is considerably higher than that required by this formula, so that they are generally represented by the formula $(C_6H_{10}O_5)_n$.

We have already examined the formation of the characteristic blue colour when iodine acts on starch (Exp. 344 (ii)).

Exp. 404.—Boil starch with dilute sulphuric acid, and test the solution with Fehling's solution and with iodine.

We note that the starch gradually forms a clear solution containing a sugar which can be identified as malt sugar.

There is now reason to believe that both starch and cellulose are built up of triplets of molecules of sugars of the dextrose or laevulose type, so that they may be represented as $(C_6H_{10}O_5)_{3n}$; n is probably about 12.

In the composition of all the compounds above described the ratio of $H : O = 1 : 8$ as in water; they are closely related in properties and can be readily changed one into another, and they are all grouped together in the class of *carbohydrates*. It must not be assumed, however, that they are water compounds.

358. Other Carbohydrates.—Among other bodies closely related to the sugars and belonging to the carbohydrate group may be mentioned dextrins, glycogen, and inulin.

The *dextrins* are compounds intermediate between starch and sugar, formed as an intermediate product in the action of malt on starch and in the digestion of starch in the body.

Dextrins are soluble in water, give a red colour with iodine instead of the blue of starch, and are hydrolysed to dextrose.

Glycogen is a kind of starch which is found in the animal body and which passes easily into maltose.

Inulin is a sugar found in dahlia and other tubers, which is hydrolysed into laevulose.

359. **Pentoses.**—In addition to the above carbohydrates, which are all derived from molecules containing 6 carbon atoms grouped together, other compounds are found containing groups of 5 carbon atoms; these are termed *pentoses*. Pentoses are found in gum as *arabinose*, $C_5H_{10}O_5$, and in many other products.

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